

**STUDIES ON ELECTRONICAL PROPERTIES OF DEFECTS**

**IN SILICON AND GALLIUM ARSENIDE**

**by**

**Mats Kleverman**

**Lund 1985**



**DEPARTMENT  
OF  
SOLID STATE PHYSICS**



**UNIVERSITY OF LUND  
SWEDEN**



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## **Studies on electronical properties of defects in Si and GaAs**

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This thesis is based on investigations of thermal and optical properties of some defects in Si and GaAs. The work consists of five papers, namely

- I. Electrical properties of Fe in GaAs  
(Journal of Applied Physics 54, 814 (1983) )
- II. Photo-admittance spectroscopy  
(Solid State Communications 46, 895 (1983) )
- III. Capture processes at double donors in silicon  
(Physical Review B, in press)
- IV. Photo-thermal investigation of magnesium related donors  
in silicon  
(manuscript)
- V. Absorbtion study on Beryllium doped silicon  
(manuscript)

Co-authors are H.G.Grimmeiss(I-V), P.Omling(I), L-Å.Ledebo(I),  
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## Introduction

The detailed knowledge of the physical and chemical properties of semiconductor materials is the foundation of the electronical revolution. The prosperous progress of the device development since the invention of the transistor in 1947 rely on the possibility of impurity doping in a controlled manner. By varying the defect concentration, resistivities from the insulator to metal limits are obtained. Although silicon is the most frequently used material, the development of new technologies based on e.g. III-V materials is very intensive. Contemporary III-V materials are used for high speed and optical devices.

Defects can introduce bound states in the band gap. These localized states are classified as shallow or deep energy levels according to their energy position in the gap. Unintentionally introduced deep defects may cause severe failures in the intended behaviour of the devices. This may even be the case at very low defect concentrations. Furthermore, deep defects may open nonradiative recombination paths resulting in e.g. a drastic degradation and lowering of the life time of e.g. laser diodes caused by local heating in the vicinity of the defects. In some applications, deep centers are used in the device manufacturing in order to tailor a certain desired property of the component. Au or Pt doped silicon is commonly used to facilitate a decrease of the switching time of transistors.

The papers comprising this thesis are dealing with two different semiconductors, silicon and gallium arsenide. In the following two sections some particular properties of these materials are discussed

## The Materials

Silicon, a group IV element, has  $[\text{Ne}]3s^2 3p^2$  atomic electron configuration. The crystal bonds, being the well known  $sp^3$  hybridized orbitals, are completely covalent. Si crystallizes in diamond structure, consisting of two fcc sublattices displaced  $1/4$  along the space diagonal. In Fig.1 the one electron  $E(\mathbf{k})$  band structure for high symmetry directions of the first Brillouin zone (Fig.2) is presented.

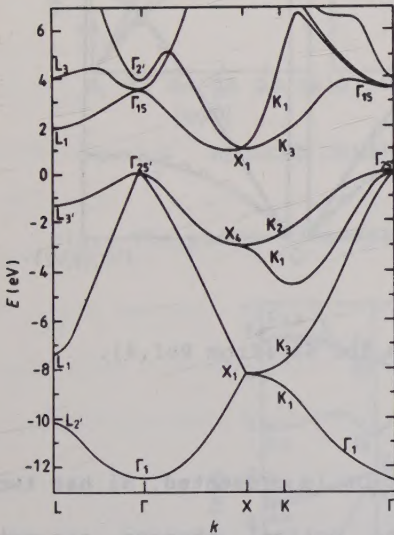


Fig.1 Electronic band structure of Si (from Ref.1).

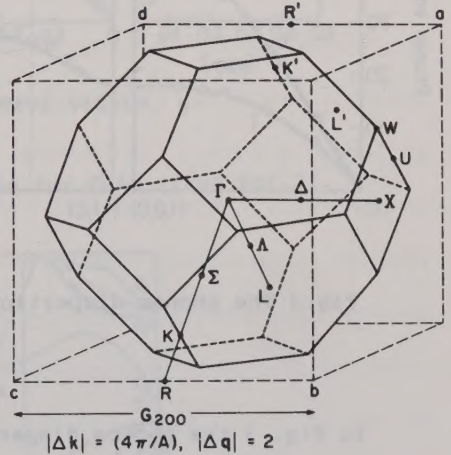


Fig.2 The first Brillouin zone for zinc blende and diamond structure (from Ref.2).





Silicon has an indirect fundamental band gap and there are six equivalent conduction band minima located  $0.85 \cdot 2\pi/a$  in  $\langle 100 \rangle$  and equivalent directions. Both the top of the valence band and bottom of the conduction band are anisotropic. The lowest conduction band is s-like and nondegenerate and the highest valence band is p-like and 3 fold degenerate, excluding spin degeneracy. The valence band degeneracy is partly lifted by spin orbit interaction and splits into an upper 4 fold and a lower 2 fold degenerate band (including spin). The energy separation is the spin orbit energy<sup>3</sup>  $\Delta_{so} = 42.62$  meV.

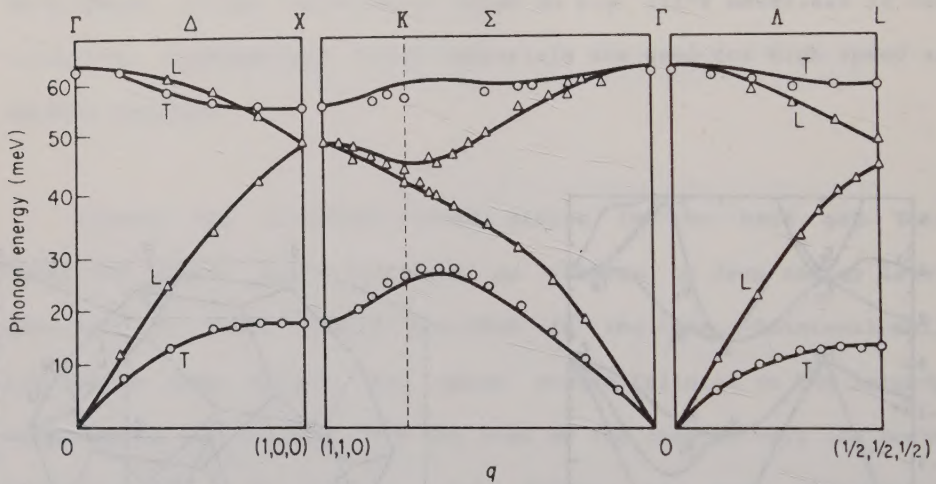


Fig.3 The phonon dispersion relation for Si (from Ref.4).

In Fig. 3 the phonon dispersion relation is presented. Si has two identical atoms per unit cell and the optical phonons are not optically active since no dipole moment exists.

Gallium arsenide is a member in the III-V family of technically important semiconductor materials for high speed and optical devices. The crystal has zinc blende structure similar to the diamond structure but the fcc sub lattices consists entirely of Ga or As atoms. Ga and As have  $[\text{Ar}]4s^2 4p$  and  $[\text{Ar}]4s^2 4p^3$  electron configuration, respectively.



The crystal bonds have both covalent and ionic bond character. The first Brillouin zone is identical to that of silicon (Fig.2) and the character of the upper valence band and the lower conduction band is similar to the Si structure. GaAs has a direct band gap in the  $\Gamma$  point and in Fig.4 and Fig.5 the dispersion curves for phonons and electrons in GaAs are presented, respectively.

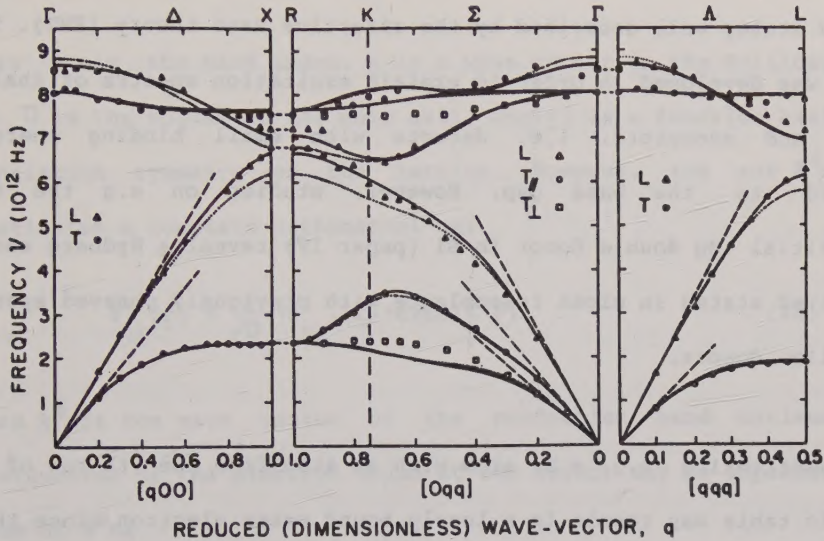


Fig.4 The phonon dispersion relation for GaAs (from Ref.2).

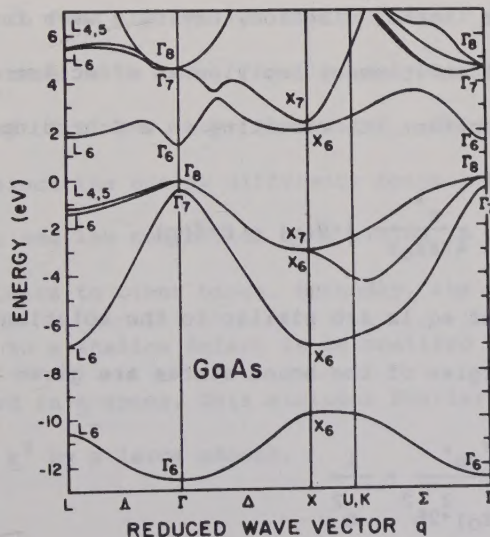


Fig.5 Electronic band structure of GaAs (from Ref.2).

## Models of the systems

The centers studied in this thesis all have a ground state influenced by a short range potential. In addition, to this potential, some centers have a long range Coulomb potential which gives rise to excited states well described by the effective mass theory (EMT). This theory was developed in order to explain excitation spectra of shallow donors and acceptors, i.e. defects with small binding energies compared to the band gap. However, studies on e.g. the deep interstitial Mg double donor in Si (paper IV) reveal a Rydberg series of excited states in close resemblance with previously observed spectra of shallow donors.

Substituting e.g. a Si atom with an atom from the Vth row of the periodic table may result in a loosely bound extra electron since there is one electron in excess after completing the  $sp^3$  orbitals. Intuitively, this situation is close to the atomic hydrogen problem. However, the extra bound electron, having a wave function  $\Psi(\underline{r})$ , is moving in a crystal environment implying an effective mass ( $m^*$ ) and a static dielectric constant ( $\epsilon$ ) resulting in a Schrödinger equation

$$\left\{ \frac{-\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{4\pi\epsilon\epsilon_0 r} \right\} \cdot \Psi(\underline{r}) = E \cdot \Psi(\underline{r}) \quad (1a)$$

The solutions of eq.1a are similar to the solutions of the H atom problem and the energies of the bound states are given by

$$E_n = \frac{Z^2 \cdot e^4 \cdot m^*}{(4\pi\epsilon\epsilon_0)^2 \cdot 2\hbar^2} \cdot \frac{1}{n^2} \quad (1b)$$

A more accurate theory than that implied in eq.1a was developed by Luttinger and Kohn<sup>5</sup>. The wavefunctions of the perfect crystal  $\Phi_{n\mathbf{k}}$  constitute a complete orthonormal set of basis functions.

$$\Phi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \cdot U_{n\mathbf{k}}(\mathbf{r}) \cdot \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (2a)$$

where  $n$  is the band index,  $\mathbf{k}$  is a wave vector in the Brillouin zone and  $\Omega$  is the volume of the unit cell.  $U_{n\mathbf{k}}(\mathbf{r})$  is a function having the translation symmetry of the lattice. However, the set  $\Phi_{n\mathbf{k}}^0$  also constitutes a complete orthonormal set

$$\Phi_{n\mathbf{k}}^0(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \cdot U_{n\mathbf{k}^0}(\mathbf{r}) \cdot \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (2b)$$

where  $\mathbf{k}^0$  is the wave vector of the conduction band minimum. The wavefunction of the electron bound at the defect may be expanded into a sum of  $\Phi_{n\mathbf{k}}^0$

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_n F_n(\mathbf{k}) \cdot \Phi_{n\mathbf{k}}^0(\mathbf{r}) \quad (3)$$

In order to find the Fourier coefficients  $F_n(\mathbf{k})$  in eq.3 several approximations have to be made. Firstly, only terms from the nearest conduction band i.e.  $n=0$  are considered. This is a reasonable approximation since the energy difference between the ground state of a shallow donor and the conduction band minima is small compared with the energy distance to other bands. Secondly, the wave function of an electron bound to a shallow defect is delocalized in real space and hence, localized in  $\mathbf{k}$ -space. This excludes Fourier coefficients with  $\mathbf{k}$  differing from  $\mathbf{k}^0$  by a large amount.



These approximations lead to a problem of finding an envelope function  $F(\underline{r})$  (the inverse Fourier transform of  $F_n(\underline{k})$ ) determined from the effective mass equation

$$\left\{ \frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{4\pi\epsilon\epsilon_0 r} \right\} \cdot F(\underline{r}) = E \cdot F(\underline{r}) \quad (4)$$

$F(\underline{r})$  varies slowly over one unit cell and the total wavefunction is given by

$$\Psi(\underline{r}) = F(\underline{r}) \cdot \Phi_{ok0}(\underline{r}) \quad (5)$$

Since eq.4 is similar to the hydrogenic Schrödinger equation, the eigenvalues are determined from eq.1b and the eigenstates may be classified in accordance with the H atom. For donors in e.g. Si eq.4 has to be modified because of the anisotropic effective mass to

$$\left\{ -\frac{\hbar^2}{2} \left[ \frac{1}{m_t} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{m_l} \frac{\partial^2}{\partial z^2} \right] - \frac{e^2}{4\pi\epsilon\epsilon_0 r} \right\} F(\underline{r}) = E \cdot F(\underline{r}) \quad (6)$$

where  $m_l$  and  $m_t$  are the longitudinal and transverse effective masses, respectively. No analytical solutions to eq.6 exist and a variational method has been applied to calculate the energy spectrum<sup>6-7</sup>. The Hamiltonian has cylindrical symmetry and parity (l odd or even) and the projection of  $\underline{L}(m)$  on the z-axis is a good quantum number. The eigenstates are built up of states of the same parity and m, but in spite of this mixing it is customary to label the states according to the atomic notations nlm. States with the same n but different l are nondegenerate. Moreover, states differing in |m| are split.

EMT donor wave functions are at least six fold degenerate in Si due to the six equivalent conduction band minima. Eq. 6 is then modified to a linear combination<sup>8</sup>

$$\Psi(\underline{r}) = \sum_{j=1}^6 \alpha_j \cdot F(\underline{r}) \cdot \Phi_{0\mathbf{k}}^j(\underline{r}) \quad (7)$$

The higher excited states extend over a large volume of the crystal and for these states it is a good approximation to neglect disturbances from any short range potential. However, the EMT energy for the donor ground state may in several cases be about one order of magnitude too small compared with experimental data<sup>7,9</sup>. This chemical shift or central cell correction is due to the short range potential having appreciable strength only in the vicinity of the impurity site. This short range potential reflects the local symmetry of the defect. A single substitutional impurity in silicon has tetrahedral ( $T_d$ ) symmetry and  $\Psi(\underline{r})$  is split into states belonging to different irreducible representations of the  $T_d$  point group.

The  $A_1$  state has equal weights in the sum of Bloch waves from the 6 conduction band minima leading to a nonzero amplitude at the impurity site, and thus, this state is strongly affected by the short range potential. E and  $T_2$  representations have nodes at the impurity site implying a smaller deviation from the 1s EMT energy for 1s(E) and 1s( $T_2$ ) than for 1s( $A_1$ ). This is verified in several experimental investigations.

In Fig.6 a level scheme of a donor in Si is presented and dipole and/or symmetry allowed transitions are indicated. In paper II a new space charge technique is described, suited for optical investigation of such transitions.

Photo conductivity measurements on some Mg related donor centers are presented in paper IV. The binding energies of the excited states follow the predicted EMT energies. However, some discrepancies are observed which may be introduced by the short range potential.

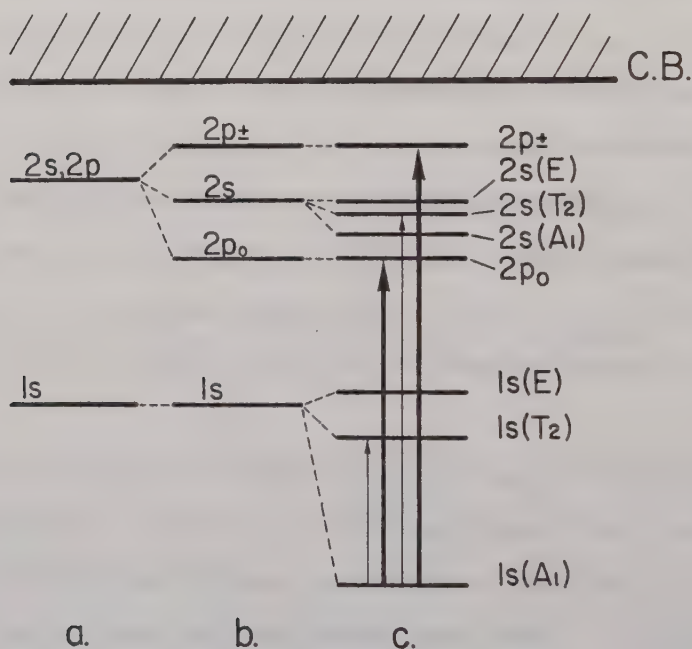


Fig.6 Donor states according to EMT. a) isotropic effective mass b) anisotropic effective mass and c) valley orbit interaction included.

Dipole and symmetry allowed transitions (thick arrows).  
Symmetry allowed transition (thin arrows).



It is the complex nature of the top of the valence band in crystals having diamond or zinc blende structure that leads to a more complicated theoretical treatment of shallow acceptor states than in the case of donor states. The top of the valence band is split into a 4 fold ( $\Gamma_8^+$ ) and a 2 fold ( $\Gamma_7^+$ ) degenerate band (including spin) due to the spin-orbit interaction and the transformation properties of the valence band states in the  $\Gamma$  point are in accordance with the cubic double group  $\hat{O}_h$  (for e.g. Si and Ge). As in the donor case, a shallow acceptor state is described by a product between a Bloch wave ( $\Phi_j^\Gamma$ ) and an envelope function  $F_j$  which is determined from the 6 coupled differential equations

$$\sum_{k'} D_{k'k}(-i\nabla) F_{k'}(\underline{r}) + \frac{e^2}{4\pi\epsilon\epsilon_0 r} F_k(\underline{r}) = E \cdot F_k(\underline{r}) \quad (7)$$

$D_{k'k}(-i\nabla)$  is a 6x6 matrix operator, specific of the host material, reflecting the symmetry of the valence band in the  $\Gamma$  point. Hence,  $F_j$  transforms according to irreducible representations of  $\hat{O}_h$ . In EMT  $F_j$  may be approximated by hydrogen like functions s,p,d,... which are basis functions of  $O_3$  and transform according to  $D_0^+$ ,  $D_1^-$ ,  $D_2^+$ , ..., respectively. The transformation properties of the acceptor wave function is then determined by the direct product  $\Gamma(F_j) \times \Gamma(\Phi_j^\Gamma)$  which is reduced to irreducible representations of  $\hat{O}_h$ .

Another approach<sup>10,11</sup> has been developed more recently where the terms in  $D_{k'k}(-i\nabla)$  with spherical symmetry have been isolated from the cubic terms. This leads to a more convenient classification scheme of acceptor states in close resemblance with atomic and nuclear states. The contribution to the energy due to the cubic terms<sup>12</sup> may be treated by perturbation theory for most materials. In the strong spin orbit coupling limit, valid for e.g. Ge, the total angular momentum  $\underline{F} = \underline{L} + \underline{J}$  is

a good quantum number. Bound states originating from the  $\Gamma_8^+$  valence band have  $J=3/2$  and an therefore an S state has  $F=3/2$  and is designated  $S_{3/2}$  and a P state has  $F=5/2, 3/2, 1/2$ . For a given principal quantum number, three P-states exist. The cubic term in the Hamiltonian<sup>12</sup> splits  $P_{5/2}$  into a  $P_{5/2}(\Gamma_7^-)$  and a  $P_{5/2}(\Gamma_8^-)$  state. In Fig.7 is a tentative interpretation<sup>10</sup> of the lowest states is given for an acceptor in Si and classified in terms of the cubic and spherical model.

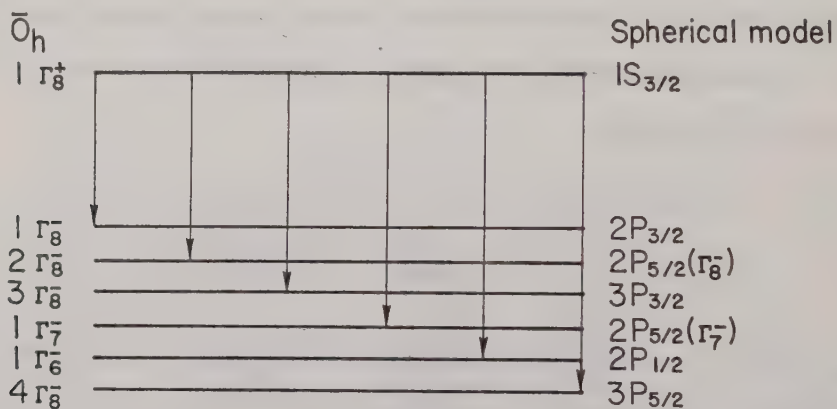


Fig.7 The lowest transitions from the  $P_{3/2}(\Gamma_8^+)$  acceptor ground state to the odd parity excited states in Si. The classification is in accord with the spherical model and with  $\hat{O}_h$ .

The EMT theory schematically presented above fails to describe centers with binding energies of the same order as the band gap. Such centers are commonly referred to as deep centers. The origin of this failure is the invalidity of the approximations made above. Differences in the atomic properties between the host and the impurity atom gives rise to a short range potential. However, if the strength and form of the impurity potential are known, it is possible to determine the bound state energies through an expansion in Bloch waves. Since the impurity potential is rarely known, a proper way to

handle the deep level problem is to find eigenstates and eigenvalues from a self consistent method<sup>13-16</sup>.

The properties of the transition metal impurities in semiconductors seems to entirely depend on the outer incomplete d shell. A d state splits into an e- and a  $t_2$ -state in  $T_d$  symmetry. For a defect on substitutional site a  $t_2$ -state has much larger overlap with the  $sp^3$  hybrid orbitals than an e-state and the electronical repulsion is then smallest for an e-state. Consequently, the ground state is an e state. For an interstitial impurity the interaction with the not completely screened positive ions favours the  $t_2$  state and the level scheme is opposite to the substitutional defect (Fig.8).

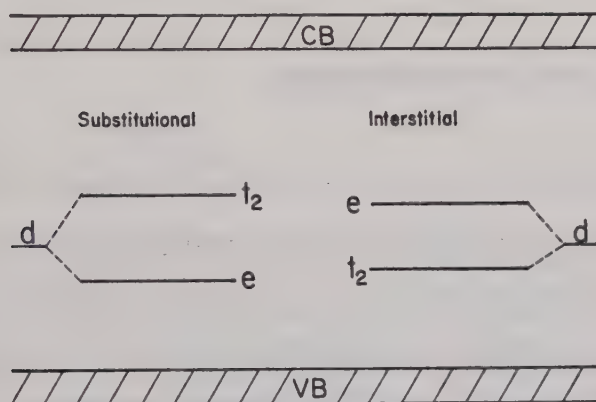


Fig.8 One electron states for a d-electron impurity on substitutional or interstitial  $T_d$  site in Si.



The transition metal Fe in GaAs has been studied in paper I. The photo ionization cross section for holes was investigated and the energy split between the e and  $t_2$  state was deduced. Furthermore, Fe has also been studied<sup>17-18</sup> in the  $\text{GaAs}_{1-x}\text{P}_x$  alloy system where the energies of the e and  $t_2$  states have been determined for different compositions x. The result showed that the Fe acceptor level was not pinned to any band and the energy position could be interpreted to be more or less related to the vacuum level. This is in agreement with previous experimental<sup>19,20</sup> and theoretical<sup>21</sup> investigations.

The electronic properties of deep levels are often characterized by parameters such as emission and capture rates. A short survey in the importance of these parameters is given in the following sections.

### **Thermal emission and capture processes**

Insight into emission and capture processes in semiconductors is of great interest in both applied and basic semiconductor physics. The lifetime of excess charge carriers is very sensitive to the recombination properties of intrinsic and extrinsic defects. Different devices have different needs to become optimized. In some applications, such as high speed switching devices, the lifetime has to be very short. In optical devices e.g LED:s and laser diodes it is of great importance to avoid all non-radiative recombination processes competing with the radiative recombination. This demands a very long lifetime of excess carriers implying a very low concentration of undesired impurities.

In a classical paper, Shockley and Read<sup>22</sup> deduced an analytical expression connecting the emission rate ( $e$ ) and capture constants ( $c$ ) by using the principle of detailed balance. The interpretation of the binding energy has since then changed<sup>23, 24</sup> and  $e$  and  $c$  are connected through this expression

$$e_{n,p} = c_{n,p} \cdot g_{n,p} \cdot N_{c,v} \cdot \exp(-\Delta G_{n,p}/kT) \quad (9)$$

$\Delta G_{n,p}$  is defined as the change in Gibbs free energy when emitting an electron or a hole, respectively, excluding contributions from the electronic degeneracies,  $g_{n,p} \cdot N_{c,v}$  is the effective density of states in the conduction band and the valence band respectively.  $\Delta G_{np}$  can be calculated from the measured temperature dependence of  $e_{np}$  and  $c_{np}$ . Moreover, the change in vibration entropy can be calculated from the thermodynamical relation

$$\Delta G_{np} = \Delta H_{np} - T\Delta S_{vib} \quad (10)$$

since the change in enthalpy,  $\Delta H_{np}$ , can be determined from the slope of an Arrhenius plot of  $\exp(-\Delta G_{np}/kT)$ . The change in vibration entropy is caused by the frequency change of the vibration modes. It was recently shown<sup>24</sup> that only local modes contribute to  $\Delta S_{vib}$ .

There has been extensive experimental and theoretical efforts made in the investigation of capture processes at defects in semiconductors. These processes are discussed in terms of radiative, cascade, multiphonon, and Auger capture or a combination of two or several processes. In an emission process, energy has to be added to the bound electron or hole. This energy is supplied by interaction with e.g phonons or photons. In the inverse process, when an electron

or a hole is captured by a center, energy is gained by the center. This energy has to be dissipated from the vicinity of the center.

The ground state energy of a deep center largely exceeds the highest bulk phonon energy. This excludes nonradiative recombination by single phonon emission. The electron-phonon interaction between localized phonons and bound electrons or holes may introduce a nonradiative path for recombination. This interaction is commonly visualized by the concept of configuration coordinate diagram (Fig.9) giving the total energy in terms of electronical and vibrational energy. The system is usually treated within the adiabatic approximation. This means that the lattice is considered to be static during any electronical excitation.

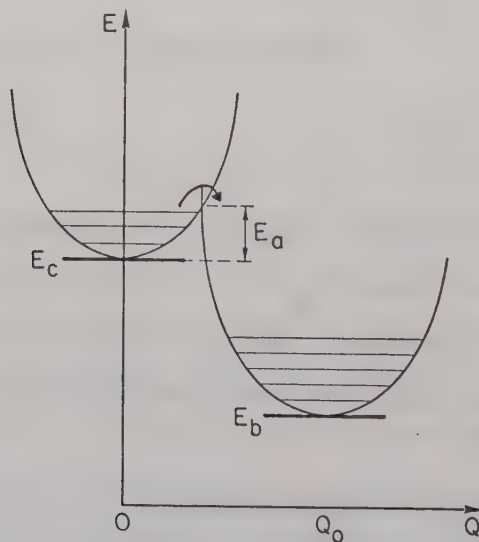


Fig.9 Configuration coordinate diagram showing the electronical and elastic energy as a function of  $Q$ .  $E_b$  and  $E_c$  are the electronical energy for the bound and free electron, respectively.  $E_a$  is the energy barrier in the capture process.

In a multi phonon emission<sup>25-26</sup> process (MPE) the charge state of a center can be altered by a multipel emission of phonons. In order to be captured the charge carrier has to surmont the energy barrier  $E_a$  and in the high temperature limit the capture cross section ( $\sigma$ ) follows a temperature activated expression:  $\sigma = \sigma_{\infty} \cdot \exp(-E_a/kT)$ .

Indications for MPE process was obtained when studying the hole-capture at singly positively charged chalcogen centers in Si (paper III). These measurement clearly showed that different hole-capture processes have to be considered for neutral and charged chalcogen centers. In the case of neutral centers it could be shown that the hole-capture is governed by an Auger type capture process.

Several Auger processes have been investigated<sup>27</sup>, mostly the technically important band-to-band Auger process wich is belived to control the lifetime of charge carriers at high doping levels in semiconductor devices. In paper III an other type of Auger process was investigated. This type of Auger process involves centers able to bind two or more charge carriers<sup>28</sup> as e.g. the chalcogens S, Se, and Te in silicon.

Sulfur, Selenium, and Tellurium form different donor centers in Si. At substitutional site S, Se, and Te are double donors. A double donor has three charge states, neutral, singly positively, and doubly positively charged state, designated  $D^0$ ,  $D^+$ , and  $D^{2+}$  respectively. When neutral, two electrons are bound at the center. In capture processes such as e.g MPE or radiative capture the capture





## Electron-phonon interactions

In solids, the electron and phonon systems are linked together through electron-phonon interactions and studied in e.g luminescence and bound to bound excitations. In paper IV and V a resonant electron-phonon process has been investigated in Mg and Be doped silicon. It is usually referred to as a Fano resonance process<sup>29-31</sup> which was first studied in atomic spectra<sup>32</sup>, where continuum states are resonant with bound two electron states.

When a continuum state and a bound electron-phonon state have the same energy, the excitation from the ground state has two energetic degenerate final states (Fig.11).

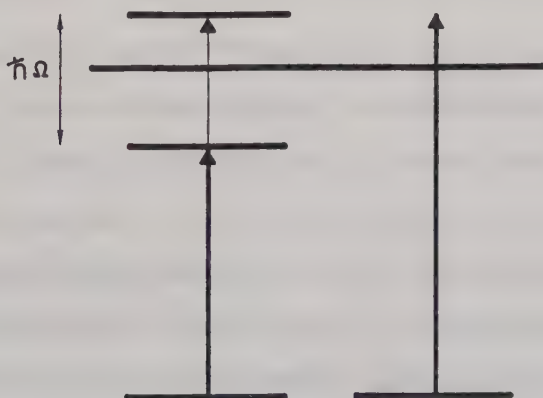


Fig.11 Fano resonance process (see text).

Any interaction between the final states, may give rise to a resonance structure in the continuum part in e.g an absorption spectra. The phonons involved are determined from symmetry rules and conservation of the crystal momentum. For donors, both inter- and intra-valley phonons are allowed but only the gLO and fTO intervalley phonons have been observed to interact<sup>27,30</sup>. The  $O^{\Gamma}$  phonon has only experimentally

been verified to be involved in the Fano process at acceptors<sup>29,34</sup>.

The allowed direct bound to bound transitions are determined from dipole and symmetry considerations. In the Fano resonance process resonances involving transitions to bound states not allowed in e.g. absorption have been observed. This gives an opportunity to determine binding energies of e.g. the valley orbit split states.

### Experimental techniques

The development of experimental methods for studying optical and thermal properties has resulted in a great variety of sophisticated measuring techniques.

Junction space charge techniques<sup>35-36</sup> can be tailored to be suitable in many experimental situations. The capacitance of e.g. a pn diode is determined by the charge within the space charge region. This enables a very sensitive detection of emission and capture processes causing a change in the net charge in the space charge region. Thermal and optical processes can be studied independently by some experimental precautions. The capacitance signal when emitting or capturing charge carriers is an exponential transient under certain experimental conditions. The time constant  $\tau$  of the transient is easily determined. When studying e.g. electron emission  $\tau$  is related to the emission rate  $e_n$  by  $1/\tau = e_n$ .

Deep Level Transient Spectroscopy<sup>37</sup> ( DLTS ) is an improvement of single shot capacitance transient techniques for the study of thermal processes. The output signal from a DLTS setup is due to capacitance transients having a proper timeconstant given by the so called time

window. As the temperature is scanned, different centers contribute to the output signal at different temperatures. A DLTS spectrum thus gives a "finger print" of the electrically active defects in the material investigated. The emission rate at the DLTS peak position is determined from the timewindow. By changing the timewindow the peaks appear at some other temperature and the emission rates at other temperatures may be determined. Such measurement techniques are particularly suitable to study electronic transitions involving deep centers since all transitions can easily be identified. This was one of the reasons why DLTS techniques were used to study Auger type capture processes in paper III. These measurements proved unambiguously that single substitutional chalcogens donors in Si are double donors.

The spectral dependence of the photoionization cross section is studied by several techniques such as absorption, photoconductivity, photo capacitance transients. In paper II an additional technique, photo admittance spectroscopy ( PAS ) is suggested.

In absorption measurements all excitations caused by photons are detected. This is not the case in photo conductivity (PC) measurements where only excitations leading to a free electron or hole contribute to the signal. A bound to bound excitation is not detected in a PC measurement unless the excited carrier is thermally excited into the band. This photo thermal process may give a severe temperature broadening of lines especially for deeper excited states which, in order to contribute to the signal, demand a relatively high temperature. It is possible to overcome this inconvenience by introducing a second center in the sample having a smaller binding energy than the center to be studied. A suitable choice of shallower centers are those having the continuum part of the spectra in the same



energy range as the discrete line spectra of the deeper center. Then bound to bound excitations at the deeper center decreases the photon flux available to the shallower center and the transitions are detected as a decrease in the PC signal.

In absorption a relatively high concentration of active centers is needed. Charge carriers bound to equivalent centers in the crystal interact if the overlap of the wavefunctions is appreciable. This causes a substantial broadening of the lines in highly doped samples and sets an upper concentration limit. The absorption signal is generally small and decreases the signal to the detector by a small amount. However, this is not satisfactory since the signal to noise ratio can be very low. In a PC measurement the sample is a detector of its own and a substantial increase of the signal to noise ratio is obtained.

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# Electrical properties of Fe in GaAs

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GaAs has been doped with Fe by diffusion and by liquid-phase epitaxy. The deep level introduced has an optical cross section for excitation of holes to the valence band with one threshold at 0.46 eV and another at about 0.85 eV. By combining those data with previous measurements of internal transitions between the ground state and an excited state, the level position in the gap is established. Optical excitation of electrons to the conduction band is below the limit of detection. The cross section for capture of electrons is nearly temperature independent with a value of about  $10^{-19}$  cm<sup>2</sup> at 200 K, and the thermal activation energy for emission of holes is 0.54 eV after  $T^2$  correction.

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## I. INTRODUCTION

Insight into the electronic properties of iron-related centers in GaAs is of interest both for the fabrication of devices and for a more basic understanding of *d*-shell impurities in semiconductors.

Iron doping of GaAs has been suggested as a method for the production of semi-insulating epitaxial layers,<sup>1,2</sup> which are often used for device isolation in integrated circuits. On the other hand, Fe added inadvertently during crystal growth may be responsible for thermal conversion of heat-treated semi-insulating substrates.<sup>3</sup>

To aid in a better understanding of transition metal impurities in semiconductors, a number of experimental<sup>1-20</sup> and theoretical<sup>21-23</sup> investigations have been performed on iron in GaAs. Most experimental studies have concentrated on internal transitions within the *d* shell by measuring optical absorption, emission, or Electron Paramagnetic Resonance (EPR). The free Fe atom has an outer shell configuration  $3d^6 4s^2$ . When introduced into GaAs, paramagnetic resonance shows that the Fe atom is incorporated substitutionally in the Ga sublattice, and has a deformed state of a  $3d$  wave function for a free atom.<sup>17</sup> This is in agreement with results obtained by other authors<sup>12,18</sup> also by EPR. Further confirmation is given by Mössbauer effect measurements.<sup>14</sup> In binding, three electrons are lost, resulting in a  $3d^5$  configuration (this is sometimes referred to as  $Fe^{3+}$ ). When binding an electron, a  $3d^6$  configuration is created ( $Fe^{2+}$ ).

A  $3d^6$  orbital with tetrahedral symmetry is split into a  $^5E$  ground state and a  $^5T_2$  excited state by the crystal field. When spin-orbit interaction is taken into account, these states are further split.<sup>5,24</sup> The latter splitting, however, turns out to be a minor perturbation. The internal transition between  $^5E$  and  $^5T_2$  has been observed both in absorption<sup>5,8</sup> and in luminescence,<sup>2,3,10,16,19</sup> with a major central peak at 0.37 eV. Much detail has been found in luminescence measurements in the analogous systems GaP:Fe<sup>25</sup> and InP:Fe.<sup>16</sup>

From measurements of EPR, absorption and luminescence caused by the internal transition, it cannot be decided whether or not the impurity has an energy level in the band gap. For example, Ni in GaAs has been seen in EPR,<sup>26</sup> but so far no corresponding deep energy level has been observed in the gap.<sup>27</sup> In some previous experimental studies, sugges-

tions as to the energy positions of Fe levels in GaAs have been made. In most of these studies, a level at about  $E_v + 0.5$  eV is observed,<sup>1,4,7,9,11,13,19</sup> whereas some also find a level at about  $E_v + 0.35$  eV.<sup>9,11</sup> The scatter in published data is considerable. The purpose of this paper is therefore to report on thermal and optical transitions between impurity levels and the band edges in Fe-doped GaAs. We have studied optical cross sections, thermal emission rates, and capture cross-sections. Furthermore, the experimental results are correlated with what is at present known about internal transitions within the *d* shell in the  $d^6$  state.

## II. EXPERIMENTAL DETAILS

### A. Sample preparation

Fe-doped  $n^+p$  and  $p^+n$ -junctions were prepared by liquid phase epitaxy (LPE) and  $p^+n$ -junctions by diffusion. The  $n^+p$  diodes were made in a slider graphite boat on a  $p^+$  substrate. The starting temperature for growth was 850 °C and the cooling rate 20 °C/h. Five at. % Fe was put in the Ga melt, which resulted in a deep-level concentration of  $10^{14}$  cm<sup>-3</sup>. The shallow level dopant was Ge for the *p* layer ( $2 \times 10^{16}$  cm<sup>-3</sup>), and Sn for the  $n^+$ -layer ( $2 \times 10^{18}$  cm<sup>-3</sup>). Reference samples grown with no Fe in the melt had a total deep-level concentration of less than  $10^{11}$  cm<sup>-3</sup>. Early attempts to dope with Fe failed, presumably because of oxidation of the Fe by oxygen in the Ga melt. When the Fe was added to the melt after bake-out for several hours in hot hydrogen gas, the doping was reproducible. It is, however, probably not meaningful to define a distribution coefficient from these experiments, since the final concentration of deep Fe-levels seems to be determined mainly by the cooling rate due to out diffusion.  $p^+n$  LPE diodes were made in a similar way on  $n^+$  substrates.

The diffused diodes were made on a VPE  $nn^+$  substrate (BDH Chemical Ltd.), the *n* layer being Te-doped with a free-carrier concentration of  $10^{16}$  cm<sup>-3</sup>. A  $p^+nn^+$  structure was made by diffusion of Zn in a quartz ampoule from a Zn:Ga source saturated with GaAs. Typical diffusion parameters were 5 min at 710 °C, which gave a junction depth of 1.4 μm. On part of the wafer, about 50 nm of Fe was evaporated. The coated wafer was put into an evacuated quartz ampoule containing a Ga melt saturated with GaAs

to inhibit As losses from the wafer during diffusion. To serve as reference sample, an uncoated wafer was given similar treatment. The diffusion time was 2 h, and the temperature varied from 700 to 750 °C. The ampoules with the samples were rapidly pulled out from the furnace and allowed to cool in air. Diffusion temperatures from 725 to 750 °C all resulted in a deep-level concentration of  $1 \times 10^{15} \text{ cm}^{-3}$ . A DLTS profiling<sup>28</sup> for samples diffused at the higher temperatures showed that the deep-level concentrations were constant throughout the depletion regions in contrast to samples diffused at 700 °C. The DLTS spectrum of a sample diffused at 750 °C is shown in Fig. 1, together with the spectrum of the reference sample. The additional peak at 215 °C is probably due to contamination with Cu. LPE samples had only the Fe-related 297 °C peak.

### B. Measurement techniques

Various forms of junction space-charge techniques were used for the electrical investigations of our samples. For the study of thermal emission rates of holes, both deep-level transient spectroscopy (DLTS)<sup>28</sup> and dark-capacitance single-transient techniques<sup>29</sup> were used. The results are shown together with previously published data in Fig. 2. The experiments were performed in *n*-type and *p*-type materials using  $p^+n$  and  $n^+p$  junctions. No significant difference was observed.

The capture cross section of electrons from the conduction band to the  $3d^5$  state and its temperature dependence were measured by DLTS techniques<sup>28</sup> in the temperature region where the emission rates fall within the DLTS window. In a lower temperature range, we used a technique with multiple short filling pulses,<sup>30,31</sup> as shown in Fig. 3. The experiment must be made in a  $p^+n$  sample with a large initial

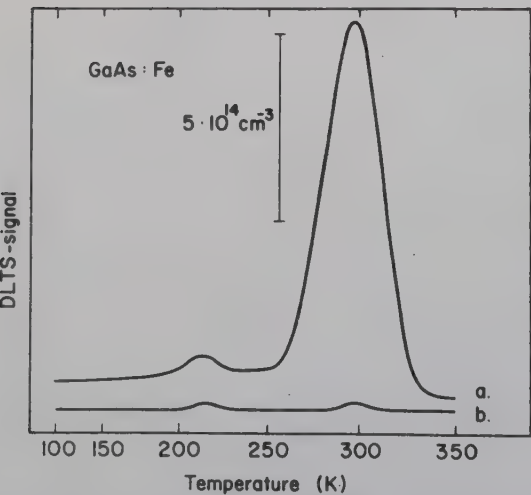


FIG. 1. (a) The DLTS spectrum for an Fe-diffused  $p^+n$ -junction. (b) The DLTS spectrum for the reference sample. Background Fe and Cu (with a peak at about 215 K) probably diffuse from the substrate during heat treatment. LPE samples had no background impurities. The rate window for the spectrum was  $77 \text{ s}^{-1}$ .

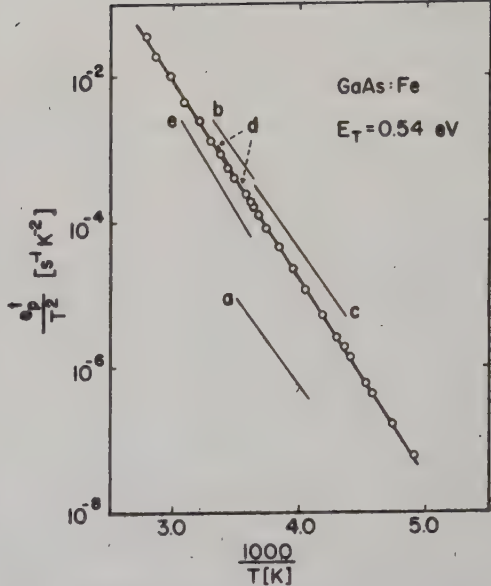


FIG. 2. Thermal emission rates vs inverse temperature:  $\circ$ -our data, *a*-Ref. 3, *b*-Ref. 1, *c*-Ref. 44, and *d*, *e*-Ref. 15. Although all the data (except *a*) are very close to ours, some of them have considerably different activation energies due to the small range of temperature used. Known temperature dependences have been corrected for by the  $T^2$  factor. The uncorrected energy value is 0.59 eV.

occupancy of holes. This was achieved by current injection using a 1.5-V forward pulse during 0.5 ms, which saturated the levels with holes. After restoration of the 3-V reverse bias, the free-carrier tail was allowed to reach equilibrium with the centers closest to the neutral region. The reverse voltage was then reduced from 3 V to 0 V by 5- $\mu\text{s}$  long pulses with a repetition frequency of 0.5 Hz. The initial exponential decay is followed by a slower decay owing to the capture of electrons from the free-carrier tail at 0 V. Because of this base-line variation, it is difficult to determine a steady-state value for the relevant part of the transient. A difference method was therefore used for the evaluation of capture transients, with evaluation of only the first part of the transient where the relative contribution from tail effects is small:

$$\begin{aligned} \Delta C_k &= C_{k-1} - C_k \\ &= [C(0) - C(\infty)](e^{-(k-1)\Delta t/\tau} - e^{-(k\Delta t/\tau)}) \\ &= [C(0) - C(\infty)](e^{(\Delta t/\tau)} - 1)e^{-(k\Delta t/\tau)}. \end{aligned} \quad (1)$$

Here  $C_{k-1}$  and  $C_k$  are the capacitance after pulse  $k-1$  and pulse  $k$ , respectively. If the logarithm of  $\Delta C_k$  is plotted vs  $k\Delta t$ , a straight line with slope  $-1/\tau = -c_n n$  is obtained (Fig. 3). The free-carrier electron concentration was determined from a plot of values of  $1/C^2$  vs  $V$ . The temperature dependence of the capture cross section is plotted in Fig. 4.

The optical emission rate of holes was determined by photocapacitance transients (Fig. 5). The cross section was evaluated using the time constants for the full transients, or by using the initial slope of the transients. The total capacitance change as a function of the photon energy (Fig. 6) was

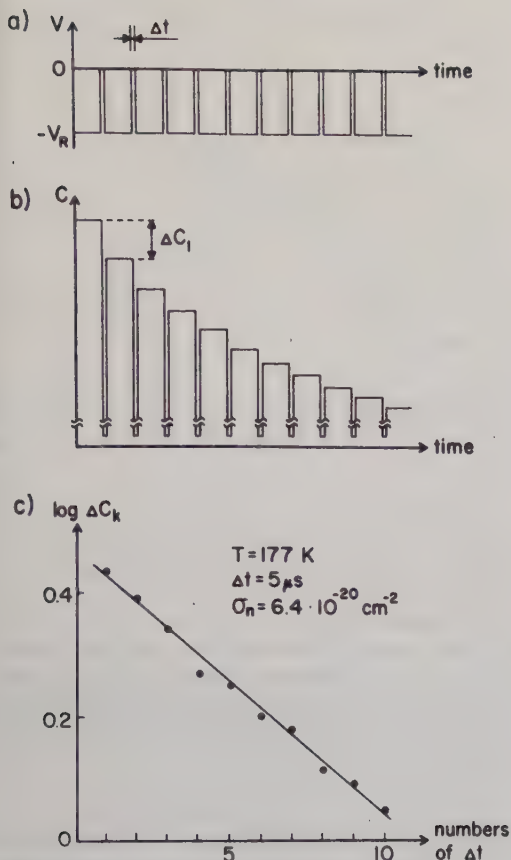


FIG. 3. Diagram showing the measurement technique for the electron capture cross section. (a) the pulse sequence, (b) the observed capacitance signal. The capacitance meter is disconnected during the pulses, and (c) the plot used for determination of the capture cross section.

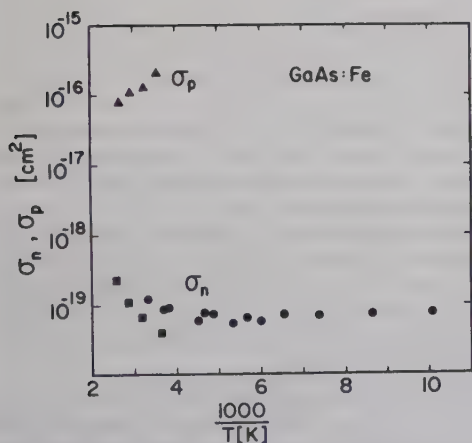


FIG. 4. Capture cross sections of electrons and holes vs inverse temperature. ● denotes data from this work, whereas ■ and ▲ are as determined by Lang and Logan.<sup>7</sup>

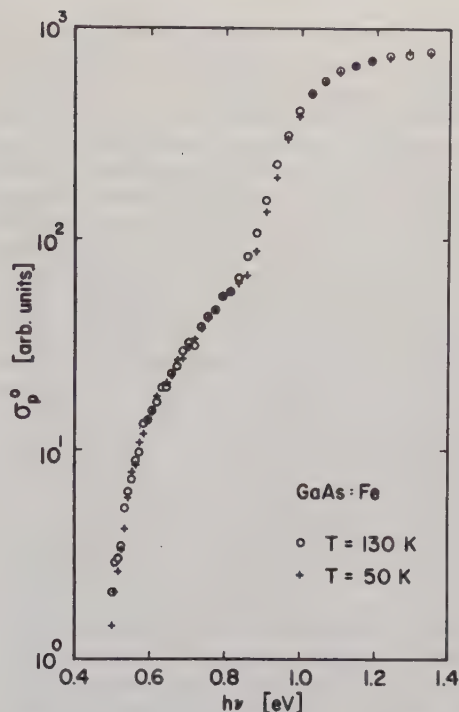


FIG. 5. The photoionization cross section for the excitation of holes to the valence band. The two curves have been arbitrarily normalized, but the difference in absolute values is within the experimental uncertainty.

also recorded. To compensate for variations in the width of the excitation region with varying excitation rates,  $e_p^0$  was kept constant by varying the voltage to the lamp of the monochromator.

### III. DISCUSSION

The spectrum of the optical cross section  $\sigma_p^0$  (Fig. 5) exhibits a threshold at about 0.5 eV, and a second one at

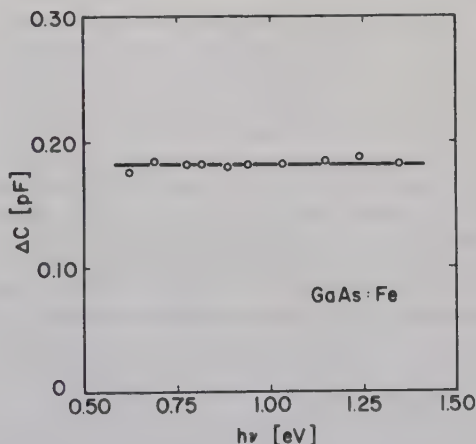


FIG. 6. Amplitude of the capacitance transient as a function of photon energy at 130 K. The straight line is drawn as a guide to the eye.



about 0.85 eV. Such a spectrum may in principle be caused by two different defects, one with a level at  $E_v + 0.5$  eV, and another with a level at  $E_v + 0.85$  eV. This was in fact suggested by Kitahara *et al.*<sup>9</sup> who obtained a spectrum similar to the one in our Fig. 5 by photoconductivity measurements. It is, however, very difficult to decide from photoconductivity measurements whether a spectrum contains contributions from one or several defects. If their interpretation of the spectrum is correct, the amplitude of the capacitance transient should change at 0.85 eV. To investigate this, we recorded the full optical capacitance transient and the capacitance amplitude determined, as described in Sec. II. From Fig. 6, it follows that the capacitance amplitude is constant over the full range of photon energies. From this and the fact that the capacitance transients were single exponentials, it can be concluded that only one kind of impurity is responsible for the full spectrum in Fig. 5, and the structure in the spectrum must be found in the optical matrix element or in the density-of-states of the impurity or the valence bands. The spin-orbit splitting causes steps in the density-of-state of the valence band. The splitting in GaAs has been determined to be 0.34 eV.<sup>32</sup> A second threshold in the spectrum of  $\sigma_p^0$  may therefore be expected at a photon energy of about 0.85 eV. However, this effect is not seen for other impurities in GaAs (Cu<sup>27</sup>, EL<sup>23</sup>, A and B<sup>34</sup>). Nor is it observed for GaP:Fe<sup>35</sup> and InP:Fe<sup>36</sup> since in these materials the energy separation between the thresholds is similar to that in GaAs:Fe, although the spin-orbit splitting is much smaller (82 mV for GaP and 110 mV for InP<sup>30</sup>). We therefore attribute the second threshold to optical excitation from the valence band to the excited  $d^6$  state,  $^5T_2$ .

The data presented in Fig. 5 are sufficiently accurate to permit a fit to theoretical photoionization cross sections. The fit obtained is shown in Fig. 7, where the transition to the ground state has been fitted with a simple theoretical model,

$$\sigma^0(h\nu) = 1.0 \times 10^{-16} \frac{(h\nu - 0.46)^{5/2}}{h\nu^3}. \quad (2)$$

The units are  $\text{cm}^2$  and eV.

Eq. (2) corresponds to a vertical forbidden transition<sup>37</sup> in a semiconductor with parabolic bands. We have not been able to fit the second threshold with any simple relevant function, since the second branch of the spectrum depends on the validity of the extrapolation of the first branch. For the high-photon energies used, it is reasonable to assume that the valence bands are no longer parabolic. The threshold of the second branch will, however, not be markedly changed by small variations in the first branch. The energy value of the threshold of the second branch is in good agreement with a splitting of 0.37 eV. A somewhat different value of the splitting could also be understood due to preferential optical excitation from the valence band to other states of the  $^5T_2$  group than those involved in internal transitions.

The ratio between the absolute values for the two branches of the photoionization cross section may be intuitively understood by considering the overlap of  $^5E$ ; respectively,  $^5T_2$  states with the valence band  $sp^3$  hybridized orbitals. The  $s$  part of the valence band does not give any

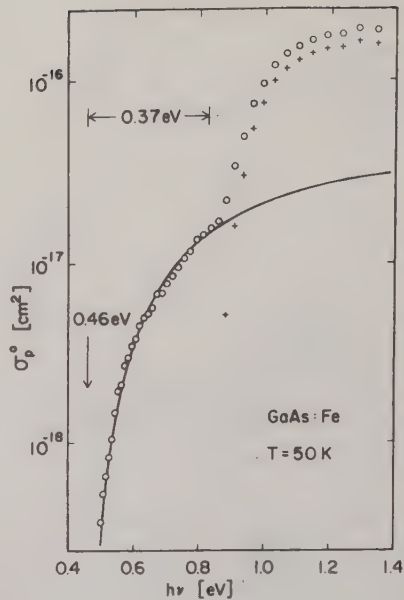


FIG. 7. Absolute value of the optical cross section  $\sigma_p^0$  at 50 K. The circles are experimental values and the solid curve is the fit obtained using Eq. (2). The crosses show the second branch as determined by subtracting the extrapolation of the first branch from the experimental values. The threshold value of 0.46 eV obtained using Eq. (2) and the splitting between  $^5E$  and  $^5T_2$  (0.37 eV) are also indicated.

contribution with  $^5E$  or  $^5T_2$ . The  $p$  states overlap only with  $^5T_2$ . The inclusion of some  $d$  nature in the valence band away from  $k = 0$  may well lead to the experimentally observed photoionization cross section.

The energy difference between the two thresholds is very close to what is seen in the line spectra of optical absorption and optical emission.<sup>2,3,5,8,10,16,19</sup> From the thermal data in Fig. 2, it follows that the ground state is about 0.5 eV above the valence band edge. We therefore suggest the level scheme presented in Fig. 8. Electronic relaxation from the  $^5T_2$  state to the  $^5E$  state within the impurity atom is expected to occur very rapidly, leaving practically no atoms left in the excited state, even for very strong optical excitations. The level scheme presented in Fig. 8 is similar to those suggested for Fe in InP<sup>36</sup> and Fe in GaP.<sup>35</sup> Nordquist *et al.*<sup>19</sup> used selective excitation to obtain the optical cross section for transitions from the valence band to the  $^5T_2$  state, and suggested a level scheme similar to our in Fig. 8. But they did not attempt any quantification of the photoionization threshold. Another important addition to previous investigations is our experiment leading to Fig. 6, convincingly demonstrating that both branches of the photoionization cross section (Fig. 7) are due to the same defect.

An unusual property of the Fe level is that the optical cross section for the excitation of electrons from this level to the conduction band is very small. In fact, it is so small that we have not been able to observe it. We can therefore only estimate its upper limit which, from steady-state photocapacitance measurements<sup>38</sup> is  $10^{-20} \text{ cm}^2$  at 1.3 eV. This is about

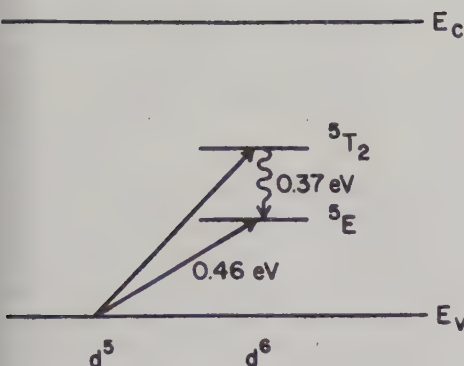


FIG. 8. Level scheme suggested by the results in this paper. The energy value 0.46 eV is the optical threshold energy. The splitting of the states due to spin-orbit effects is not included in the figure.

four orders of magnitude smaller than for many other photoionization cross sections for transitions to the conduction band in GaAs (*A* and *B*,<sup>34</sup> Cu,<sup>39</sup> EL2<sup>33</sup>). It is unlikely that large lattice relaxation is the reason for the very small value of  $\sigma_n^0$ , since no indication of such relaxation is seen for transitions to the valence band. Symmetry arguments may be used to explain the difference. In contrast to other supposedly *d*-orbital impurities such as Cu and Cr, which both have measurable transitions to the conduction band<sup>39</sup> and,<sup>40,41</sup> respectively, the symmetry of the Fe site seems to be strictly  $T_d$ .<sup>17</sup> Cu and Cr are slightly shifted from the tetrahedral position to  $C_{2v}$ <sup>42</sup> and  $D_{2d}$ ,<sup>43</sup> respectively. For purely tetrahedral symmetry, selection rules may strongly inhibit *d* orbital to conduction-band *s*-like orbital transitions.

According to the level scheme in Fig. 8, the electrons are captured into a neutral center [ $d^5 + e^- \rightarrow (d^6)^-$ ]. No influence of Coulomb barriers is therefore expected in the temperature dependence of the capture cross section for electrons. We have not been able to verify the data published by Lang and Logan,<sup>7</sup> and even though we observe some indications of the start of a temperature dependence at high temperatures, the slope is less than that reported by these authors. Instead, the main feature of our measurement is the lack of any temperature dependence of the capture cross section for electrons.

The activation energy for the thermal emission of holes  $\sigma_p^0$  is presented in Fig. 2 together with previous data published by other authors. Small errors in the temperature measurement give rise to large differences in the activation energy. For a reliable determination of the activation energy, it is therefore necessary to measure the emission over a large range of temperature. In Fig. 2, the emission rate is plotted over more than 6 orders of magnitude.

The value of 0.54 eV for the  $T^2$ -corrected thermal activation energy of holes is somewhat larger than the optical threshold at 0.46 eV. Although it is difficult to determine activation energies accurately, the uncertainty in our measurement is less than the difference between the optical and thermal values. As seen in Fig. 4, the logarithm of the hole-capture cross section vs  $1/T$ , as measured by Lang and Lo-

gan,<sup>7</sup> has a positive slope which corresponds to a "negative activation energy" of about 85 meV. It is therefore unlikely that the difference is caused by the temperature dependence of the capture cross section. Another point worthy of observation is that from the measurement of the optical cross section shown in Fig. 5, no temperature dependence is seen in the threshold, which suggests that the level is pinned to the valence band. The difference between the thermal and optical activation energies is therefore not at present understood. Similar results have been obtained for Cu<sup>39</sup> and for the so-called *B* level in GaAs.<sup>34</sup>

#### IV. CONCLUSIONS

GaAs can deliberately be doped with Fe in a controlled manner both during LPE growth and by diffusion. By studying the photoionization cross section, it has been possible to determine the position of the level in the gap and to correlate internal transitions with details in the photoionization spectrum. No temperature dependence for the energy position of the level relative to the valence band edge has been observed. The cross section for the optical excitation of electrons to the conduction band is below the limit of detection, in marked contrast to other deep-level impurities in GaAs. This can possibly be explained in terms of selection rules, excluding *d* to *s* transitions. The cross section for the capture of electrons is independent of temperature in the temperature range studied. The activation energy for the thermal emission of holes has been measured over 6 decades. The value of the  $T^2$ -corrected thermal activation energy is larger than that of the optical threshold. Fe is expected to behave in the same manner in GaP and InP, and published data indicate that the level schemes for all three compounds are similar.

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The first part of the book is devoted to a general introduction to the theory of the firm. This includes a discussion of the basic concepts of the firm, such as the production function, the cost function, and the profit function. It also includes a discussion of the various types of firms that exist in the economy, such as sole proprietorships, partnerships, and corporations.

The second part of the book is devoted to a detailed analysis of the firm's behavior. This includes a discussion of the firm's production decisions, its cost decisions, and its profit decisions. It also includes a discussion of the firm's financing decisions, such as its choice of capital structure and its choice of investment opportunities.

The third part of the book is devoted to a discussion of the firm's relationship with the government. This includes a discussion of the firm's tax obligations, its regulatory obligations, and its social responsibilities. It also includes a discussion of the firm's role in the economy and its impact on society.

The fourth part of the book is devoted to a discussion of the firm's future. This includes a discussion of the firm's growth strategies, its innovation strategies, and its sustainability strategies. It also includes a discussion of the firm's role in the future of the economy and its impact on society.





## PHOTO-ADMITTANCE SPECTROSCOPY

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We present a junction technique for measuring the spectral distribution of photoionization cross sections of centers located in the forbidden band gap of semiconductors. It is especially suitable for centers where the effect of background radiation is very disturbing and should be considered as a less expensive alternative to the Fourier photo-admittance spectroscopy technique which has been described previously.

### 1. INTRODUCTION

UNTIL RECENTLY junction techniques for studying the optical properties of centers in the band gap of semiconductors have been limited to centers deeper than about 0.3 eV. The main reason for this limitation is that centers shallower than 0.3 eV are emptied faster by room-temperature background radiation than by light from a conventional monochromator. In [1] a combined junction and Fourier technique (Fourier photo-admittance spectroscopy, FPAS) was described for which the accessible spectral region is not limited by the background radiation. In this paper we will describe a method (photo-admittance spectroscopy, PAS), which is based on the same idea but demands less advanced equipment than FPAS.

### 2. MEASUREMENT TECHNIQUE

To illustrate the method we consider a donor level in the upper half of the band gap of a  $p^+n$ -diode or an  $n$ -Schottky diode. Close to the  $n$ -edge of the depletion region there is a gaussian tail of "spill over" electrons from the neutral  $n$ -region. The tail affects the occupancy of centers at the edge of the depletion region. Electron capture from the tail changes the occupancy of the centers in competition with the emission of electrons into the conduction band. In darkness and at low temperatures the emission is governed by the background radiation since thermal emission is negligible.

When the sample is illuminated with photons of sufficient energy, emission is governed by the incident radiation. Centers close to the neutral  $n$ -region emit electrons into the conduction band in competition with electron capture from the free carrier tail. The result of the illumination is, however a decrease in the occupancy

of centers compared with the occupancy in darkness. Part of this change in occupancy gives rise to a transient current which is measurable in an external circuit (see [2]). When the light is removed the occupancy of the centers increases due to the capture of the free charge carriers resulting in a transient current in the opposite direction. As discussed in [1] any change in the occupancy occurs in a small region close to the edge (the effective region) where the capture and emission rates are of the same order of magnitude.

Closest to the neutral  $n$ -region capture dominates and the centers are therefore always filled. On the other side of the effective region capture is negligible and the centers are always empty in thermal equilibrium. If the sample is illuminated with chopped light from a monochromator, the occupancy is modulated resulting in an alternating current in the external circuit. The current measured is proportional to the emission rate times the width of the effective region (see [1]). Since the width of the effective region changes with the emission rate this introduces a slight non-linearity into the response [1]. Following the same arguments as in [1] it can be shown that the boundaries of the effective region are determined by the frequency of the chopped light and the emission rate.

The non-linear response is of minor importance when studying line spectra and results mainly in a slight increase in the half-widths of the peaks. In Fig. 1 the response vs the emission rate is presented as obtained from a simulation. The response is related to the emission rate by a power function, and it can easily be seen that the power is close to one. The non-linearity can be avoided completely by using a high-intensity lamp as a second light source superimposed on the chopped monochromatic light. The reason is that the width of the effective region is governed by the total optical emission rate, which is now nearly constant although the weak monochromatic light is scanned.

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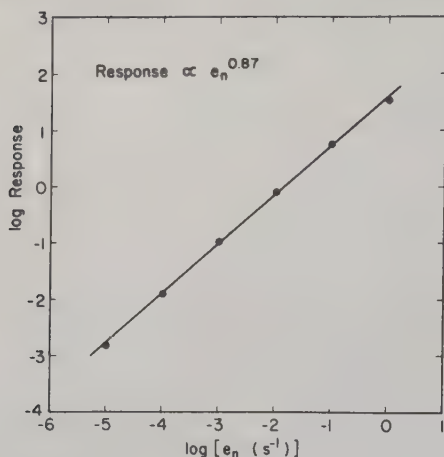


Fig. 1. Simulated response vs emission rate. The response is non-linear unless light from a constant high-intensity lamp is superimposed on the chopped monochromatic light.

The penalty which has to be paid for this improvement is a decrease in the signal-to-noise ratio. The reason is twofold. Firstly, the fluctuations of the intensity of the second light source change the width of the effective region and are registered as noise in the spectra. Secondly, the effective region decreases with increasing intensity of the high-intensity lamp resulting in a further decrease of the signal-to-noise ratio.

The resolution of the photo-admittance method depends on several parameters: The scanning speed and the resolution of the monochromator, the frequency of the chopped light, and the time constant of the detection system. When only chopped monochromatic light is allowed to illuminate the sample the resolution is reduced. This effect is due to the non-linear response with the power factor less than one (see Fig. 1) causing a lowering of peak heights and thus increasing half-widths. Furthermore, since the electric field in the effective region is not negligible, the limiting resolution is given by the broadening caused by electric field.

As pointed out in the introduction, it is often difficult to measure photo-ionization cross sections of centers with binding energies smaller than 0.3 eV with conventional junction techniques. This is due to the fact that the background radiation empties the level faster than the monochromatic light. Using PAS, the background radiation is of minor importance. The main part of the background radiation is constant and affects only the width of the effective region. It does not contribute to the current. Any chopped part of the background radiation will give rise to a small current which is constant and can consequently easily be subtracted.

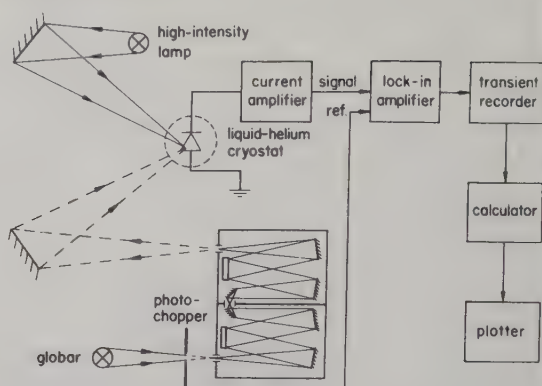


Fig. 2. Experimental set-up. As discussed in the text the high-intensity lamp is optional.

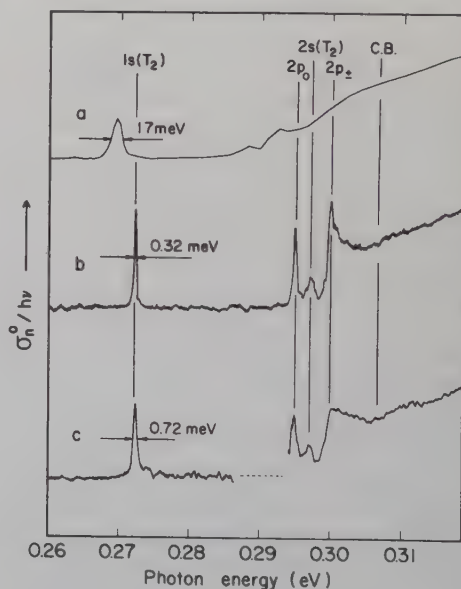


Fig. 3. Spectral dependence of the photo-ionization cross section of a neutral selenium-related center in silicon measured with three different methods using the same  $p^+n$ -diode. The methods are: (a) Photocapacitance transients (the weak structure at the ionization edge is partly due to atmospheric absorption), from [4]; (b) Fourier photo-admittance spectroscopy, from [1]; (c) Photo-admittance spectroscopy (the dashed line marks the energy region where  $\text{CO}_2$  absorption is strong).

The experimental set-up is shown in Fig. 2. As the light source a scanning double-grating monochromator was used. To avoid optical excitation from the valence band to the centers, suitable filters were used. Before the measurement was made the diode was cooled to a suitable temperature and connected to a current amplifier

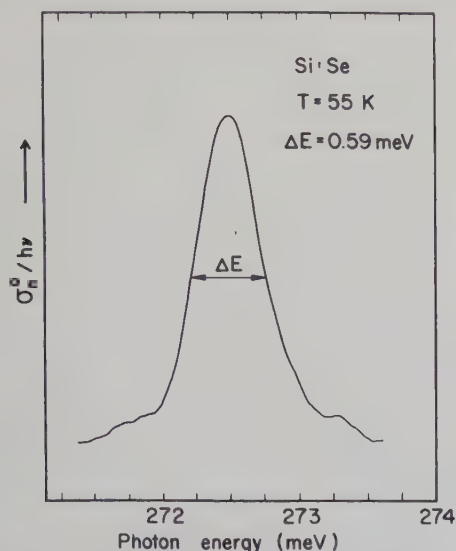


Fig. 4. The  $1s(T_2)$  peak measured using photo-admittance spectroscopy with maximal resolution.

without any external bias. During the measurement the wavelength of the chopped light from the monochromator was scanned. The output from the current amplifier was fed into a lock-in amplifier which phase-sensitively picked out the signal due to the chopped light. The spectrum was recorded on a Nicolet transient recorder and divided by the photon flux using a Hewlett Packard calculator (9825 A).

In order to illustrate the PAS method, a selenium-doped silicon  $p^+n$  diode was employed. In Fig. 3 three spectra of the photo-ionization cross section of a level, which is believed to be the neutral substitutional selenium level ( $Se^0$ ) is shown. These spectra were measured using only one sample but three different methods. Figure 3(a) was obtained by a conventional photocapacitance transient technique [4], where the influence of the background radiation was subtracted from the calculated time constant of the transients. This is sometimes very difficult, since the change of the time constant due to the illumination of the sample is only a few percent in some spectral regions. Furthermore, it is a "point by point" method and consequently very time consuming.

The spectrum in Fig. 3(b) was collected using FPAS. It is a very sensitive method with high resolution and linear response. However, the method requires sophisticated and expensive equipment. For further details, see [1]. In Fig. 3(c) the spectrum was obtained by PAS. It

can easily be seen that the quality of this spectrum is comparable to that obtained by the FPAS technique.

In order to compare the resolutions of the three different methods the resulting half-widths of the 0.27 eV peak are also shown in Fig. 3. The peak originates from transitions from the ground state,  $1s(A_1)$  to the excited state,  $1s(T_2)$ . The resolution of the  $1s(T_2)$  peak in the PAS spectrum is about twice as good as in the spectrum measured by photo capacitance transient technique. But only half as good as in the FPAS spectrum. Figure 4 shows the shape of the 0.27 eV peak when the resolution of the PAS method is maximized.

Even when the photo-capacitance transient technique can no longer be used owing to large thermal emission rates both FPAS and PAS are still applicable. The effect of the thermal emission is the same as that of the emission caused by the constant part of the background. The sensitivity is decreased and the noise is considerably increased.

### 3. DISCUSSION AND SUMMARY

The photo-admittance-spectroscopy is an optical junction technique which enables studies of electronic transitions between a level and the nearby band. Unlike the photo capacitance technique there is no need to apply a reverse bias or to optically fill or empty the centers for the investigation of optical emission processes. It is a technique which is much less time consuming than traditional optical methods and suitable for studying optical emission from centers even in the presence of disturbing background radiation.

The effective region in the depletion region is very small and close to the neutral  $n$ -region which decreases the electrical field broadening of peaks in a spectrum. Contrary to absorption measurements a layer at the surface only a few microns thick with appropriate concentration is needed.

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The first part of the book is devoted to a general introduction to the subject of the history of the English language. It begins with a discussion of the early history of the English language, from its roots in Old English to its development into Middle English and then Modern English. The author then discusses the influence of other languages on English, particularly French and Latin, and the role of the English language in the development of the English nation.

The second part of the book is devoted to a detailed study of the English language in its various stages. It begins with a discussion of Old English, which is the earliest form of the English language. The author then discusses Middle English, which is the form of the English language that developed between the end of the 11th century and the beginning of the 16th century. Finally, the author discusses Modern English, which is the form of the English language that has developed since the beginning of the 16th century.

The third part of the book is devoted to a study of the English language in its various dialects. The author discusses the differences between the various dialects of the English language, and the factors that have led to the development of these dialects. He also discusses the role of the English language in the development of the English nation, and the influence of the English language on other languages.

The fourth part of the book is devoted to a study of the English language in its various literary forms. The author discusses the development of the English language in its various literary forms, from the early history of the English language to the present day. He also discusses the role of the English language in the development of the English nation, and the influence of the English language on other languages.

The fifth part of the book is devoted to a study of the English language in its various social contexts. The author discusses the role of the English language in the development of the English nation, and the influence of the English language on other languages. He also discusses the role of the English language in the development of the English nation, and the influence of the English language on other languages.



Capture processes at double donors in silicon

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The hole-capture processes at isolated double donors in chalcogen-doped silicon have been investigated. Different steady-state and transient capacitance techniques were used. It is shown that the capture process at neutral centers is governed by an Auger-type capture process at a He-like center. The hole-capture cross sections for neutral centers are almost temperature independent and have values of about  $10^{-16}\text{cm}^2$ . The processes for hole-capture at singly ionized centers are best described as a multiphonon emission and/or a radiative process. At low temperatures the cross sections are about  $10^{-24}$ - $10^{-22}\text{cm}^2$ .



## Capture processes at double donors in silicon

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### I. Introduction

Good insight into the recombination processes of free charge carriers has long been considered important in both applied and basic research. The free carrier lifetime controls the properties of most semiconductor devices and recombination processes are frequently used to study important parameters of semiconducting materials. Recombination is often discussed in terms of radiation, cascade, multiphonon emission or Auger processes. The particles involved are photons, phonons or other charge carriers<sup>1)</sup>. In moderately doped semiconductors with indirect band gaps the lifetime of free charge carriers is generally determined by recombination via energy levels in the forbidden energy gap. These energy levels may be due to either shallow or deep centers originating from both intrinsic and extrinsic defects. The EL2 in GaAs and gold in silicon are typical examples of lifetime-controlling defects in semiconductors.

The capture of electrons into the singly charged isolated sulfur and selenium centers in silicon has recently been studied in some detail<sup>2,3</sup>). It has been shown that electron capture into these centers is probably governed by a cascade or at least a two-stage capture process via excited states. The capture cross sections describing the electron capture into the doubly ionized sulfur and selenium centers in silicon have been found to be very large and hitherto no absolute values of these cross sections have been reported.

The purpose of this paper is to report on the capture of holes at the isolated sulfur, selenium and tellurium centers in silicon. Reviews of these centers are given in Refs.4-5. In this paper it is shown unambiguously that these centres are indeed double donors. The temperature dependence of the hole-capture cross section has been studied for both neutral and singly positively charged centers. However, a major part of our study has been devoted to the hole capture of neutral centers showing that this process is governed by an Auger-type capture process.

## 2. Hole capture at neutral and repulsive centers.

A double donor has three charge states: a neutral, a singly positively charged and a doubly positively charged state. The three charge states will be denoted  $D^0$ ,  $D^+$  and  $D^{2+}$ , respectively. In the neutral state two electrons are bound to the double donor. There are two ways of changing the charge state of the center from a neutral to a singly charged state: either by exciting an electron from the center into the conduction band or by capturing a hole from the valence band as described by the following equations:



There is, however, a fundamental difference between these two processes. In the first case of electron emission the center absorbs energy whereas in the second case energy is released. The released energy has to be carried away and may trigger other processes. If the hole capture is radiative and reabsorption of the emission is not important the capture process, as described in eq.2 will result in a singly positively charged center. If, however, the hole capture is non-radiative and the released energy is carried away by another particle or particles a different final charge state may result. For example, the neutral chalcogen centers are located in the upper half of the band gap (Fig.1a) and enough

energy is released during the hole-capture process to excite the second electron of the double donors into the conduction band. The equation describing such a process is



and the process is known as an Auger-type capture process for a He-like center. The final charge state is therefore, in this case, a doubly positively charged center.

This type of Auger capture has been suggested previously as a possible mechanism for the capture of free charge carriers into deep centers but to the best of our knowledge it has never been studied experimentally. Theoretical considerations 7-10) show that the Auger-type capture process should result in weakly temperature-dependent capture cross sections in the range  $10^{-20}\text{cm}^2$  to  $10^{-14}\text{cm}^2$  which is in agreement with our results.

The  $D^+$  centers are singly positively charged and therefore repulsive to holes. Hole capture at these centres is therefore best described by different types of processes such as radiative capture processes and/or multiphonon emission (MPE) processes. Our data indicate that different hole-capture processes may occur at singly charged sulfur, selenium and tellurium donors center in silicon.



### 3. Experimental details

The samples used in this paper were either  $n^+p$  diodes or  $n^+p$  diodes in  $p^+n^+p$  transistor structures employing a  $1.5 \times 10^{15} \text{ cm}^{-3}$  boron-doped epitaxial layer as the  $p$  region (Fig.1b). The  $n^+p$  and  $p^+n^+p$  structures were doped with chalcogens by ion implantation as the dopant source and, as in the case of Se, solid state diffusion. In all cases the implantation depth was less than  $2000 \text{ \AA}$  i.e. much smaller than the depth of the  $n^+$  region. The  $n^+p$  structures were used for diffused Se and implanted Te samples. In the case of Te the  $n^+$  diffusion was done after indiffusion of the implanted Te due to the high temperature needed for the latter process.

Varying implantation procedures were employed for different chalcogens. In the case of sulfur a dose of  $5 \times 10^{14} \text{ cm}^{-2}$  at 60 keV was used for implantation of a  $p^+n^+p$  transistor structure. After deposition of a  $4000 \text{ \AA}$   $\text{SiO}_2$  layer on top of the sample in a CVD reactor at  $420^\circ\text{C}$ , the diode was diffused in an open tube furnace for 1 hour at  $1000^\circ\text{C}$  in a nitrogen atmosphere. Contact holes were then opened in the  $\text{SiO}_2$  layer by means of a photolithographic process and an aluminum layer was sputtered onto the surface, forming an ohmic contact. The electrically active sulfur concentration ( $\text{D}^0$  and  $\text{D}^+$ ) was typically  $4 \times 10^{12} \text{ cm}^{-3}$  which was about 0.4% of the shallow level concentration as deduced from DLTS measurements. The net shallow level concentration in the  $p$ -region was  $1 \times 10^{15} \text{ cm}^{-3}$ .

Selenium doping was performed at a dose of  $10^{14} \text{ cm}^{-2}$  at 100 keV. After diffusion in an oxygen atmosphere for 1 hour at 900 °C a selenium ( $\text{Se}^0$  and  $\text{Se}^+$ ) concentration of about 7% ( $5 \cdot 10^{13} \text{ cm}^{-3}$ ) of the shallow level concentration in the p-region was generally detected. The net shallow level concentration was found to be  $7 \cdot 10^{14} \text{ cm}^{-3}$ . Se doped samples were also made using a solid state diffusion procedure. A small amount of Se together with some n<sup>+</sup>p diodes and Si powder were put in a quartz ampoule. After evacuation, the sealed ampoule was put into an open furnace for 1 hour at 930°C. The shallow level concentration was about the same in both implanted and diffused samples. The  $\text{Se}^0$  and  $\text{Se}^+$  concentration was about 9% ( $6 \cdot 10^{13} \text{ cm}^{-3}$ ) of the shallow level concentration in the p-region.

Tellurium doping was achieved by ion implantation into a p-type epitaxial layer using a dose of  $10^{13} \text{ cm}^{-2}$  at 100 keV. The samples were then diffused in an open furnace at 1250 °C for 15 minutes in an oxygen atmosphere. In order to avoid too thick oxide layers the diffusion continued for 45 minutes in a nitrogen atmosphere. The n<sup>+</sup>p junction, 1.5 μm deep, was formed by phosphorus deposition at 920 °C for 20 minutes and diffusion in an oxygen atmosphere at 1000 °C for 30 minutes. The  $\text{Te}^0$  and  $\text{Te}^+$  concentration obtained using this procedure was typically 9% ( $6 \cdot 10^{13} \text{ cm}^{-3}$ ) of the shallow-level concentration. The net shallow level concentration in the p-region  $7 \cdot 10^{14} \text{ cm}^{-3}$ .

Junction space charge techniques are particularly suitable for investigations such as the ones described in this paper since they allow for a distinction between minority- and majority- charge-carrier transfer processes. Various forms of

junction-space charge techniques were therefore employed in our investigations including both transient and steady-state methods<sup>11</sup>). Emission rates were measured using Deep Level Transient Spectroscopy (DLTS)<sup>12</sup>) and single-shot capacitance techniques while capture rates were studied using both DLTS techniques and pulse-train methods<sup>3</sup>). The free hole concentration was, in all cases, determined from  $C^{-2} - V$  plots.

#### 4. Experimental results

To make sure that the chalcogen-related centers studied in our ion-implanted samples are indeed the same centers as investigated previously in diffused samples the thermal emission rate of electrons was measured for both the  $D^0$  and  $D^+$  centers in our sulfur-, selenium-, and tellurium-doped samples. Comparing our results (Fig.2) with those previously published<sup>2,3,13</sup>) on chalcogen-doped silicon it is quite evident that the same centers are formed in ion-implanted samples as in diffused samples.

The capture rates for holes were measured in  $n^+p$  diodes by first occupying the  $D^0$  and  $D^+$  centers with electrons using a minority-carrier filling pulse and then monitoring the decrease in the capacitance due to a majority-carrier pulse train of constant pulse length. The measurements were first performed on the  $D^+$  centers after thermal excitation of the first electron of the  $D^0$  centers. The hole-capture cross section,  $\sigma_p$ , was then calculated from the hole-capture rate  $\sigma_p \cdot v_{th} \cdot p$ . Where  $v_{th}$  is the thermal velocity and  $p$  is the hole concentration.

$v_{th}$  is defined by

$$v_{th} = (3kT/m_p^*)^{1/2}$$

where  $k$  is the Boltzmann constant,  $T$  is the temperature and  $m_p^* = 0.70m_e$  is the effective mass of holes. The hole-capture cross sections calculated from the capture rates measured are presented in Fig. 3. At low temperatures the cross sections for the capture of holes into the singly positively charged chalcogen centers are of the order of  $10^{-24}$  to  $10^{-22}$  cm<sup>2</sup>. The largest cross section was found for the  $S^+$  center and the smallest value was measured for the  $Te^+$  center. Whereas the cross section for the  $S^+$  center showed a pronounced temperature dependence, the hole capture into the  $Se^+$  and  $Te^+$  centers was almost independent of temperature in the temperature region studied. In order to increase the temperature region for the sulfur-doped samples, similar measurements were performed using DLTS.

Investigations performed on neutral chalcogen centers gave values for the hole-capture cross sections in the region  $10^{-17}$ - $10^{-16}$  cm<sup>2</sup> for all three chalcogens (Fig.4). The largest capture cross section was again obtained for the sulfur center while the smallest cross section was measured for the tellurium center. In all three cases only a weak temperature dependence was observed. Since the capture cross sections of holes for the  $D^+$  centers were at least three orders of magnitude smaller than those for the  $D^0$  centers, the hole capture into the  $D^0$  centers could readily be measured without any disturbance from the  $D^+$  centers. Due to the small  $S$  concentration in the  $n^+p$  diodes it



was not possible to measure  $\sigma_{pD^0}$  using the pulse-train method.

The pulse-train method gave, in all cases, a single exponential dependence of the diode capacitance on the number of pulses. To demonstrate this the time dependence of the capacitance due to the capture of holes into the  $\text{Se}^0$  and  $\text{Se}^+$  centers is shown in Fig.5 for a measurement performed at about 120 K. In both cases a single time constant was found. In order to increase the temperature range of our study the pulse-train method was followed up by DLTS measurements.

#### 5. Auger-type capture processes.

To demonstrate the different types of capture processes for holes at the  $\text{D}^0$  and  $\text{D}^+$  centers, we will now describe the DLTS measurements in more detail using selenium-doped  $n^+p$  diodes as an example. The capture of holes at  $\text{Se}^0$  and  $\text{Se}^+$  centers was studied by first applying a minority-carrier pulse to establish a certain electron occupancy of the centers, followed by a majority-carrier pulse. The length of the majority carrier pulse was increased in succeeding DLTS runs (Fig.6). For a majority pulse length of 2 ms, the electron occupancy of the  $\text{Se}^0$  center was almost negligible while the occupancy of the  $\text{Se}^+$  center was still about 50%. Plotting the logarithm of the height of the two DLTS peaks obtained for a particular rate window as a function of the majority-carrier pulse length gives similar time constants for both the  $\text{Se}^0$  and  $\text{Se}^+$  peak (Fig.7). Furthermore these time constants were very close to the time constant obtained for  $\text{Se}^0$  using the pulse-train method (Fig.5), whereas the time constants obtained for

the  $\text{Se}^+$  center shown in Fig.5 and Fig.7, differ by about seven orders of magnitude. It should be noted that the  $\text{Se}^0$  and  $\text{Se}^+$  peaks appear at different temperatures. Owing to experimental difficulties it was not possible to decrease the  $\text{Se}^+$  peak (Fig.6) further by increasing the length of the majority pulse. Not even the largest majority pulse length (2.5s) changed the  $\text{Se}^+$  peak height. Since the chalcogens form double donors two DLTS peaks of similar heights are expected if the injection pulses completely fill the  $\text{D}^0$  centers with electrons. However, owing to similar capture rates for electrons and holes for the  $\text{D}^0$  centers the highest concentration of  $\text{D}^0$  centers which can be obtained in an  $n^+p$  diode after applying a long minority pulse is about one half of the concentration of the  $\text{D}^+$  centers. It should be noted that electron capture into the  $\text{D}^{2+}$  centers is much faster than into the  $\text{D}^+$  centers and, hence,  $\text{D}^+$  centers could be generated with short minority-charge-carrier pulses without generating any  $\text{D}^0$  centers at all.

Very similar results were obtained in sulfur-doped samples as can be seen by the data presented in Fig.8 showing the DLTS spectrum of a Si:S sample. The spectrum is almost identical to the Se spectrum except that the  $\text{S}^+$  peak becomes very small for long majority pulses. Whereas the decrease in the  $\text{S}^0$  peak is described by one time constant (squares in Fig.9b) the data for the  $\text{S}^+$  peak resulted in two time constants (Fig.9a). The first time constant of Fig. 9a was obtained by subtracting the slower part of the decay from the rest of the curve (Fig.9b). The time constant of the transient obtained (full circles in Fig.9b) was very close to the time constant of the transient obtained for the  $\text{S}^0$  peak (squares in Fig.9b) and the corresponding capture

cross sections were almost identical considering the different temperatures at which the peaks occurred. The second time constant derived from the data presented in Fig.9a was about three orders of magnitude larger than the faster time constant and similar to the time constant obtained for  $S^+$  by the pulse-train method.

It should be noted that the  $D^0$  centers were obtained by filling the donors with electrons during the minority-carrier pulse. The capture of holes was then initiated by a majority-carrier pulse. Since minority-carrier injection had to be avoided during the application of the majority-carrier pulse it was not possible to increase the concentration of holes during the application of the majority-carrier pulse in that region of the space charge region which was closest to the n-region (Fig. 10). Since the  $D^0$  centers in this region could not be emptied due to the capture of holes, they always contributed to the DLTS signal irrespective of the length of the majority-carrier pulse. This is the reason why a small  $D^0$  signal in the DLTS spectrum of Fig.6 and Fig.8 was observed even for very large majority-carrier pulse lengths.

The results presented so far are best understood if it is assumed that the hole capture at a  $D^0$  center results in an annihilation of the associated  $D^+$  center i.e. that the capture of a hole into a  $D^0$  center simultaneously causes the excitation of the second electron into the conduction band transforming a  $D^0$  center directly into a  $D^{2+}$  center (eq.3). This type of hole capture is considered as an Auger-type hole-capture process<sup>7-10</sup>) which is possible if the energy released by the

hole-capture process exceeds the energy needed to excite the second electron into the conduction band. This Auger-type process does not depend on the free carrier concentration.

In order to obtain further evidence for the Auger-type hole-capture process additional experiments were performed. The total capacitance,  $C$ , of the diode was studied as a function of temperature  $T$  (Fig.11). The diode was first cooled from room temperature to 77 K under constant reverse bias. After applying a minority-carrier pulse (min. pulse, see Fig.11) which generated a certain number of  $D^0$  and  $D^+$  centers, the diode was warmed up to room temperature in the first experiment. At temperatures  $T_1$  and  $T_2$  the C-T curve (1) showed two steps owing to the thermal ionization of the  $D^0$  and  $D^+$  centers, respectively. In the second experiment (curve 2) the diode was cooled again to 77 K but this time a majority carrier pulse (maj. pulse) was applied at a temperature  $T_3$  directly after the application of the minority-carrier pulse. The pulse length  $\Delta t$  of the majority-carrier pulse was chosen to be about ten time constants of the hole capture at  $D^0$  centers in order to ensure that any electron occupancy of  $D^0$  centers could be neglected after the application of the majority-carrier pulse. It should be noted that owing to the results presented in Fig.3 and Fig.4 such a majority carrier pulse is not expected to change the electron occupancy of the  $D^+$  centers. When the temperature was raised the C-T curve showed only one step at  $T_2$  owing to the ionization of those  $D^+$  centers which were generated by the minority-carrier pulse in excess of the  $D^0$  centers. Some  $D^0$  centers close to the n-region (Fig.10) remain occupied by electrons after the majority-carrier pulse and give rise to a



small step in the C-T curve (Fig.11 curve 2). The experiment clearly showed that owing to the majority-carrier pulse the diode capacitance decreased by almost twice as much as in the first experiment due to the thermal ionization of the  $D^0$  centers.

In order to show that this decrease in capacitance was not caused by hole capture into  $D^+$  centers, a third experiment was performed (curve 3). After cooling the diode to 77 K and applying a minority-carrier pulse, the majority-carrier pulse was first applied at temperature  $T_4$  after the  $D^0$  centers were already completely ionized. No change in the C-T curve was observed compared with the first experiment showing that the majority-carrier pulse length  $\Delta t$  was short enough not to significantly change the occupancy of the  $D^+$  centers. This sequence of experiments clearly demonstrates the Auger-type capture process since in the absence of the Auger process the capacitance is expected to decrease due to the majority-carrier pulse in the second experiment by the same amount as in the first experiment. Furthermore, the experiments clearly show that the centers studied are double donors i.e. that the  $D^0$ ,  $D^+$ , and  $D^{2+}$  centers are three different charge states of the same defect.

These experiments could be performed in both sulfur- and selenium-doped silicon diodes but not in tellurium-doped samples because of the high electron emission rate of the  $Te^0$  centers at 77 K and the freeze-out of the shallow acceptor levels in the p-region below 77 K.

Since our experiments unambiguously demonstrated that the  $D^0$ ,  $D^+$ , and  $D^{2+}$  centers are different charge states of the same defect it should be possible to obtain information on one of these centers by measuring certain properties of the other center. It has already been shown that hole capture into  $D^0$  centers resulted in the annihilation of a similar number of  $D^+$  centers. This gives us the possibility of measuring the hole capture process for  $D^0$  by studying the  $D^+$  DLTS peak. Furthermore the decrease in the  $D^+$  signal of the DLTS measurements due to the majority-carrier pulse, i.e hole capture into  $D^0$ , can therefore be considered as a measure of the concentration of  $D^0$  centers at this particular temperature and time,  $\delta t$ . After applying the minority-carrier pulse the occupancy of  $D^0$  centers at a particular temperature is, however, time dependent owing to the thermal ionization of  $D^0$  centers. The time dependence of the occupancy of  $D^0$  centers at a particular temperature can therefore be measured in different DLTS experiments using constant rate windows but varying the time delay,  $\delta t$ , between the minority-carrier pulse and the majority-carrier pulse of constant length  $\Delta t$  (Fig.12). The pulse length ( $\Delta t$ ) was chosen to be short enough to ensure that no holes were captured into the  $D^+$  center during the majority-carrier pulse. Hence, plotting the decrease in the DLTS signal of the  $D^+$  peak (Fig.13) logarithmically against the time delay  $\delta t$  should result in a straight line (Fig.14) the slope of which corresponds to the thermal emission rate for electrons of the  $D^0$  center at the temperature given by the DLTS peak of the  $D^+$  signal. By varying the rate windows and, hence, shifting the peak temperature of the  $D^+$  signal the thermal emission rate for electrons,  $e_n^t$  of the  $D^0$  centers can be measured as a function

of temperature and be compared with previous measurements (Fig.2) of  $e_n^t(D^0)$  obtained by conventional techniques. Similar measurements were performed using a single-shot capacitance method. The thermal emission rates of electrons obtained for the  $S^0$ ,  $Se^0$  and  $Te^0$  centers, by studying the  $D^+$  peaks at different temperatures, are plotted in Fig.15 together with our data previously presented in Fig.2. The results clearly show that the indirect measurements give the same activation energies as already obtained by more conventional techniques. The experiments confirm once more the different charge states of a double donor and the existence of the Auger-type hole-capture process. Without any of these properties the above results could not have been obtained.

## 5. DISCUSSION

Auger capture processes at He-like centers have been discussed previously in the literature<sup>7-10</sup>) and are expected to be the dominant capture process for such types of centers. However, to the best of our knowledge only very few cases are described in the literature where this type of capture process has been studied experimentally. Non-radiative-capture processes are generally explained by either multiphonon emission (MPE) or cascade processes. In both cases the capture cross section shows a typical temperature dependence. The capture cross sections obtained for MPE processes are often rather small and increase with temperature whereas those observed for cascade processes can be large and decrease with temperature. The results presented in this paper show that Auger-type capture processes may, in principle, result in

rather large or at least - as in our case - in moderately large capture cross sections which exhibit a weak temperature dependence. Similar chemical trends are observed for both  $\sigma_{pDO}$  and  $\sigma_{pD+}$ , implying that the sulfur center has the largest capture cross section for holes and the tellurium center the smallest. This result is in agreement with previous theoretical considerations<sup>7-10)</sup> of Auger-type capture processes, showing that  $\sigma_{pDO}$  should increase with increasing binding energy of the centers if effective-mass-like wavefunctions are used. It has also been predicted that the capture cross section should only be weakly temperature dependent which is in agreement with the results obtained for  $\sigma_{pDO}$  and presented in Fig.4.

Since double donors (and acceptors) exist not only in silicon but probably also in other materials such as III - V compounds it may be possible that such centers contribute to non - radiative recombination processes to a much greater extent than hitherto appreciated.

In contrast to  $\sigma_{pSO}$ , the hole-capture cross section of  $S^+$  showed a rather pronounced temperature dependence and increased with increasing temperature. This may suggest that the hole-capture process at  $S^+$  centers is governed by a kind of MPE process. MPE-governed capture processes have two temperature limits. At high temperatures the capture cross section approaches an exponential behavior whereas at low temperatures the cross section is almost temperature independent. A theoretical model has been developed previously<sup>14)</sup> describing the temperature dependence of MPE governed capture processes. The model includes two adjusting parameters, the capture



barrier height and the dominant phonon energy. Fitting the experimental results obtained for  $\sigma_{pS^+}$  to this model (Fig.16) a barrier height of about 147 meV and a phonon energy of 18.4 meV are deduced. This implies a large Franck-Condon shift of about 0.2 eV. Considering that the model is very sensitive to the value of the fitting parameters and that previous optical spectra<sup>15)</sup> did not show any indication of such a large Franck-Condon shift, further work is needed for better insight into the hole-capture processes of charged sulfur centers. Fitting our  $\sigma_{pSe^+}$  and  $\sigma_{pTe^+}$  data to the same model required a phonon energy of about 60 meV.

It is worth mentioning that the low-temperature values of all  $\sigma_{pD^+}$  cross sections are of same order of magnitude as the radiative-capture cross sections  $\sigma_{pD^+}^r$  obtained from the photoionization cross section  $\sigma_{pD^+}^o$  using the principle of detailed balance<sup>16)</sup>.  $\sigma_{pD^+}^r$  is expected to be proportional to  $\sigma_{pD^+}^o$  when neglecting the small difference in the binding energies of  $S^+$  and  $Se^+$ . It is interesting to note that previously published values of  $\sigma_{pD^+}^o$ <sup>15)</sup> for S and Se indeed show a similar trend as the corresponding hole-capture cross sections. We have no further information on whether the hole-capture process at neutral chalcogen centers is indeed radiative.

The properties of chalcogen-doped silicon devices will be discussed in a forthcoming paper<sup>17)</sup>.

## 6. Summary

We have presented experimental evidence for Auger-type capture processes at He-like defects in semiconductors. The temperature dependence and the absolute values of the Auger capture cross sections are in agreement with theoretical estimates. Our results clearly show that the  $D^0$  and  $D^+$  centers are neutral and singly positively charged versions of a double donor. The hole capture at  $S^+$  has been discussed in terms of MPE processes and a combination of MPE and radiative capture processes. The results obtained for the hole capture process at  $Se^+$  and  $Te^+$  centers are (in the temperature region studied) close to values expected for radiative capture process.

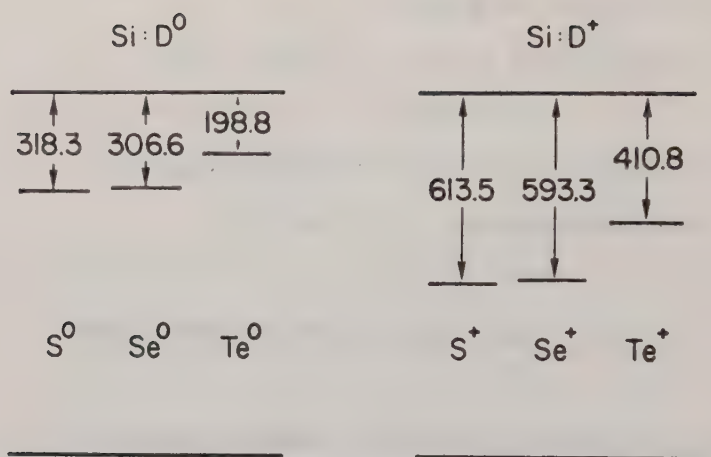
## Acknowledgements

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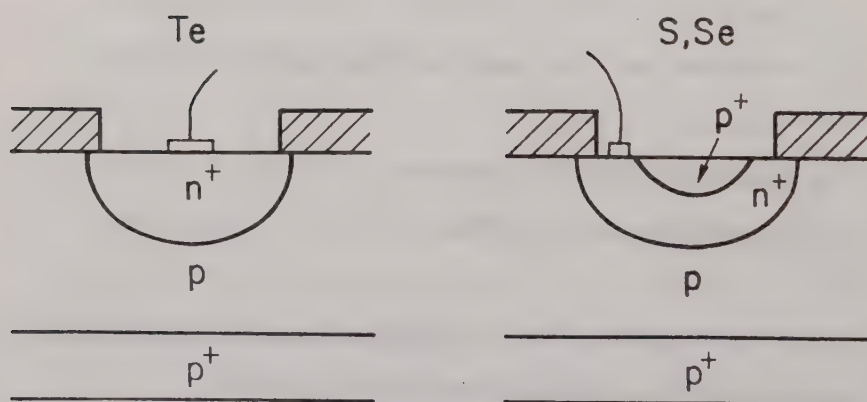
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(a)



(b)

Fig.1 a) Optical binding-energies for isolated  $\text{D}^0$  and  $\text{D}^+$  centers in chalcogen doped Si. (from Refs. 4 and 6).  
b)  $n^+p$  and  $p^+n^+p$  sample structures used in this work.



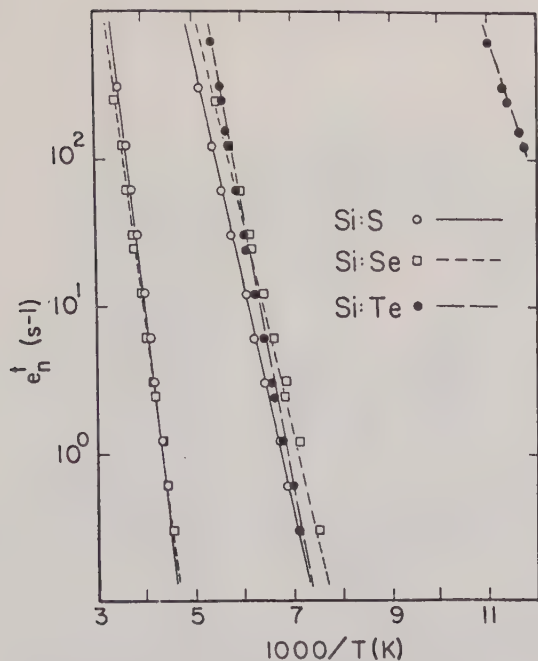


Fig.2 Comparison of thermal emission rates of electrons obtained in implanted samples and diffused samples (straight lines). The straight lines for neutral Se and Te have been extrapolated.

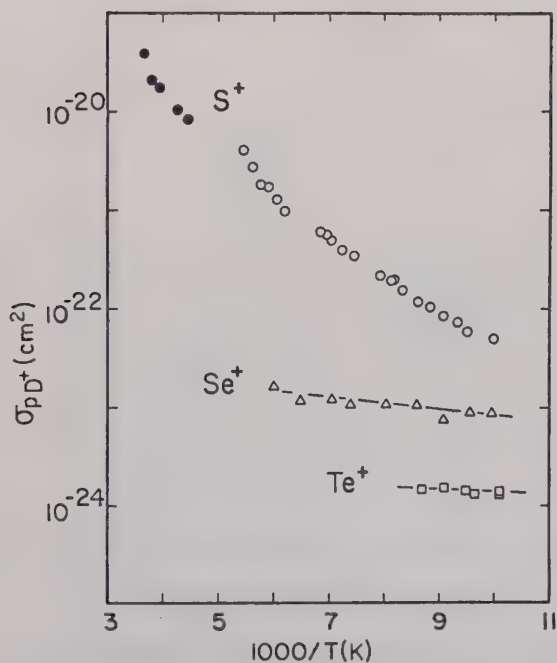


Fig.3 The hole-capture cross sections for  $D^+$  centers deduced from pulse-train and DLTS (full circles) measurements.

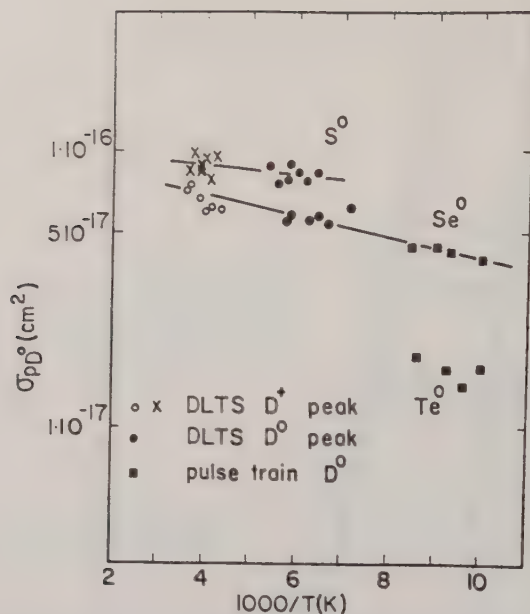


Fig.4 Hole-capture cross sections for  $D^0$  centers. Three different measurement techniques have been used: pulse-train, DLTS on the  $D^0$  peak and DLTS on the  $D^+$  peak. See text for details.

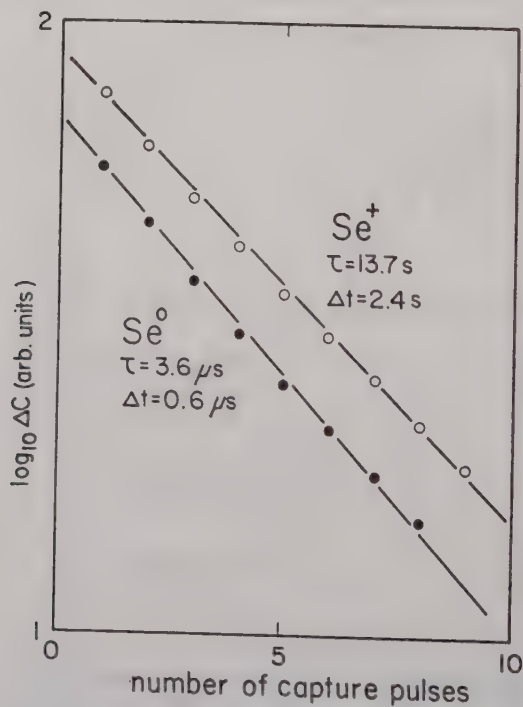


Fig.5 Transients obtained from the pulse-train technique for the  $Se^0$  and  $Se^+$  centers at about 120 K. The transients are single exponential and the time constants differ by about seven orders of magnitude.  $\Delta t$  is the constant majority-carrier pulse length.

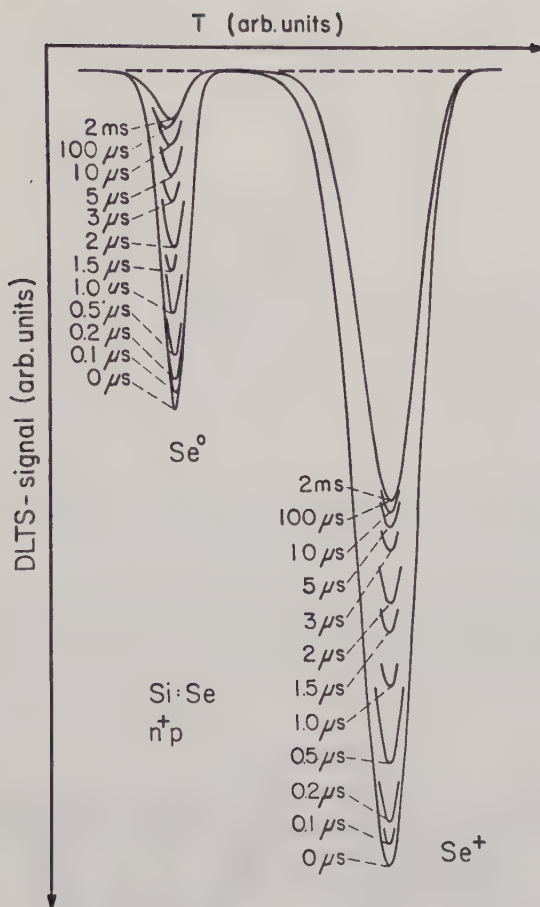


Fig.6 Hole-capture measurements on a Se doped  $n^+p$  diode showing the decrease in the DLTS peak heights with increasing majority-carrier pulse length. Note that there is no significant decrease in the  $\text{Se}^+$  peak when the pulse length is increased from 100  $\mu\text{s}$  to 2 ms.

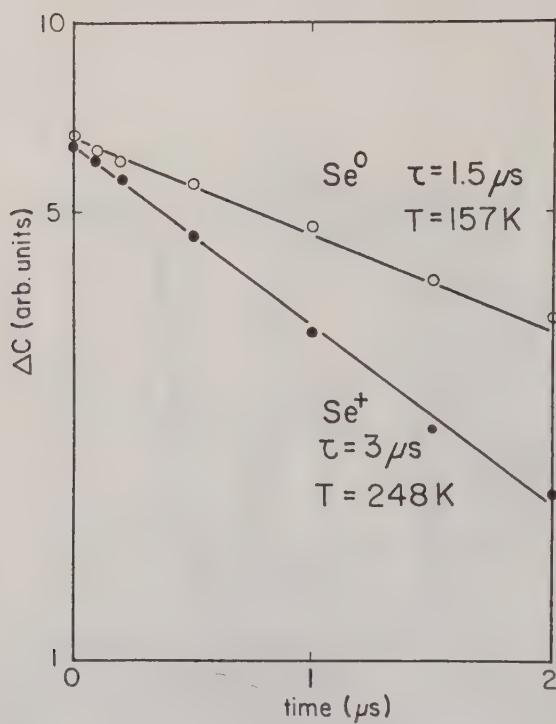


Fig.7 Plot of the  $Se^0$  and  $Se^+$  DLTS peak heights (Fig.6) versus the majority-carrier pulse length  $\Delta t$ .

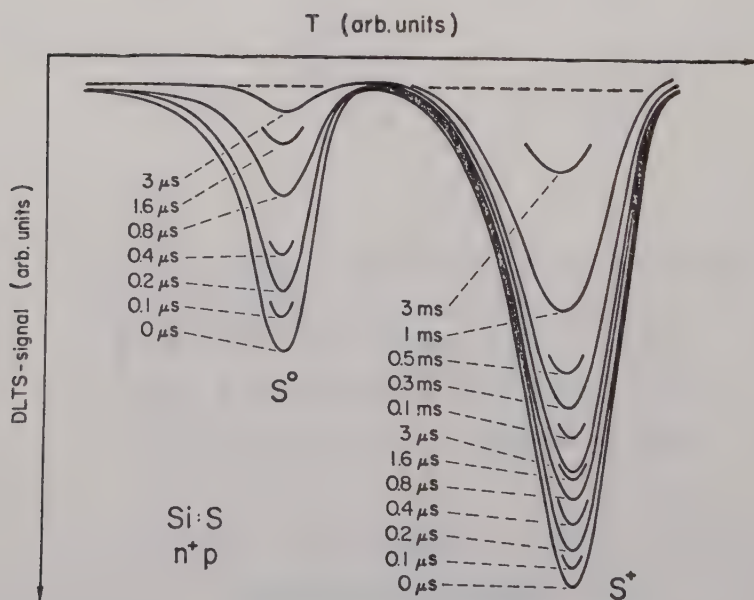


Fig.8 Hole-capture measurement on a S doped  $n^+p$  diode. Note the "break point" for the  $S^+$  peak for a  $3 \mu s$  majority-carrier pulse length.

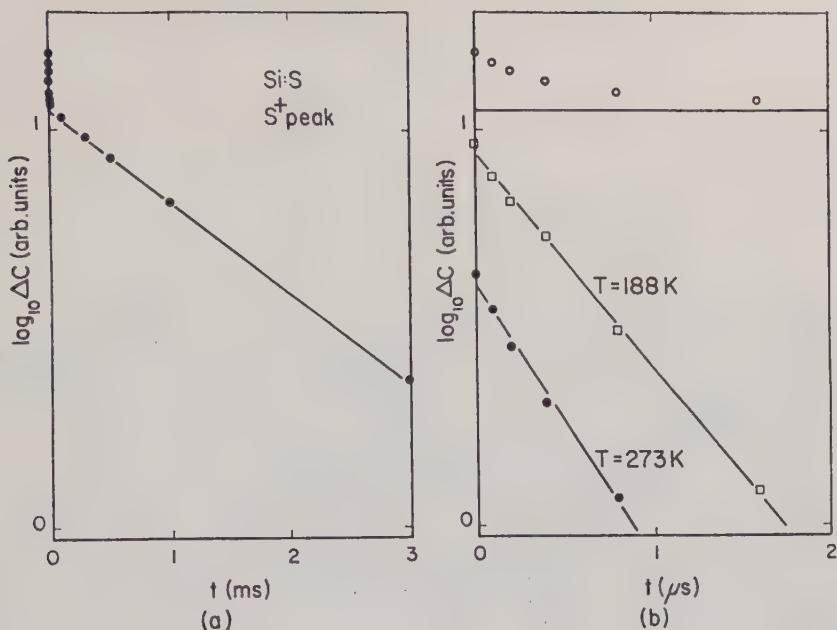


Fig.9 a) The biexponential behaviour of the  $S^+$  peak (Fig.8) due to the hole capture at the neutral sulfur center at the temperature given by the  $S^+$  peak (see text).  
b) Comparison between the transient of  $S^0$  (squares) and the first part of  $S^+$  (full circles).

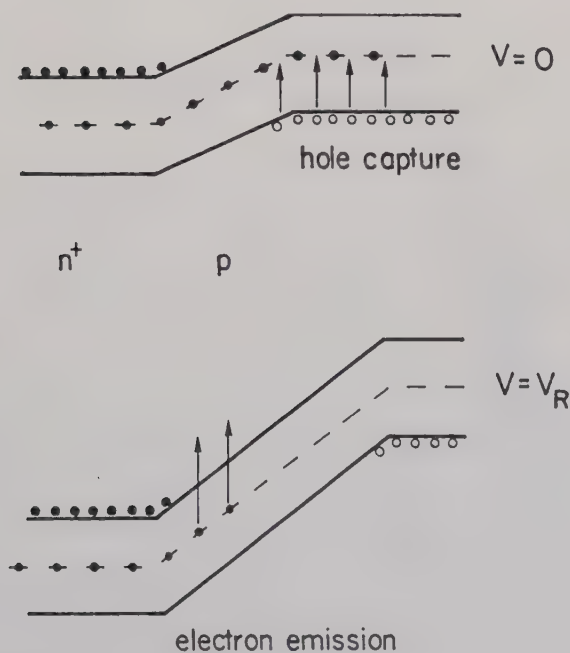


Fig.10 Simplified figure showing the origin of the residual  $D^0$  DLTS peak (Figs.6 and 8) still seen for a very long majority carrier pulse length.



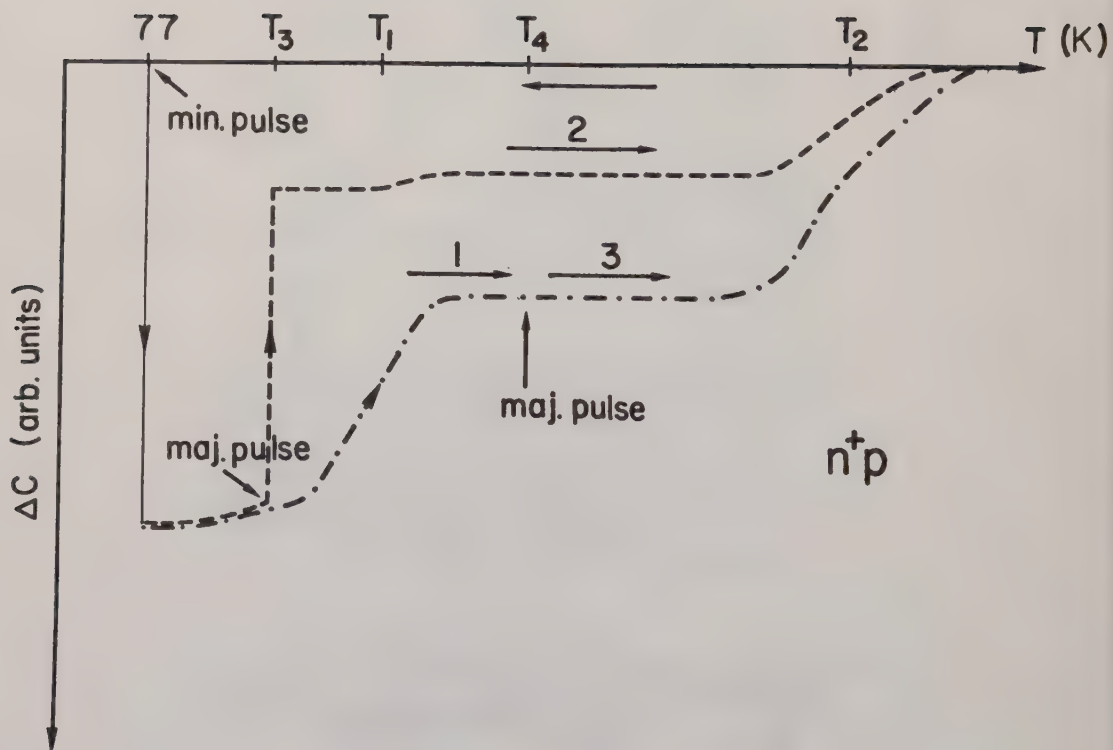


Fig.11 Junction capacitance versus temperature (see text).

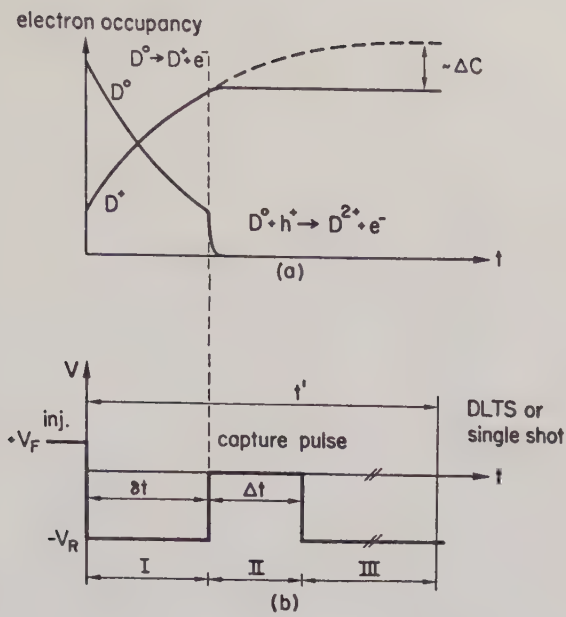


Fig.12 The time dependence of the occupancies of the  $D^\circ$  and  $D^+$  centers owing to the pulse sequence shown in b). Because of different final charge states obtained by electron-emission and Auger hole-capture at  $D^\circ$  different occupancies of  $D^+$  are obtained for varying time delays  $\delta t$ .

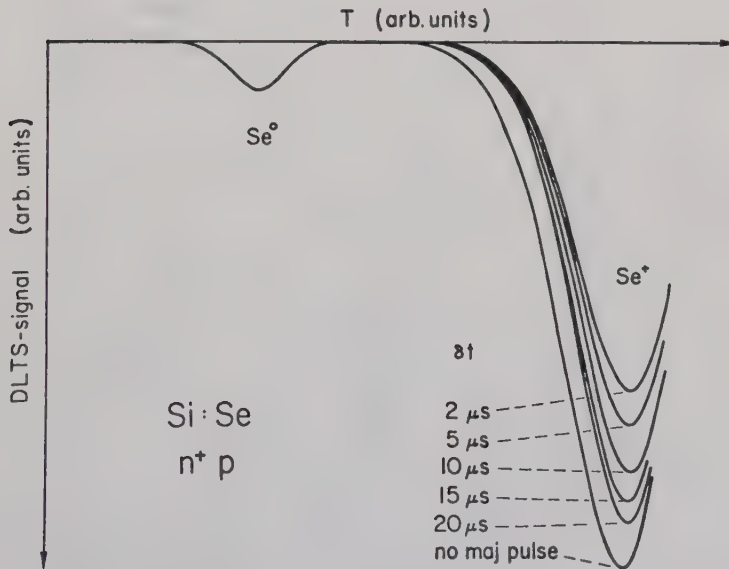


Fig.13 DLTS spectra obtained for different time delays  $\delta t$ .

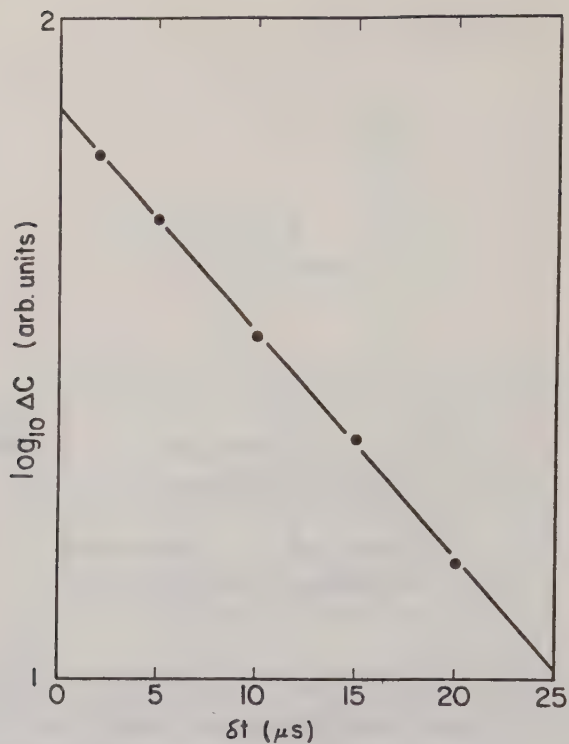


Fig.14 Plot of  $D^+$  peak in Fig.13 versus time delay  $\delta t$ .

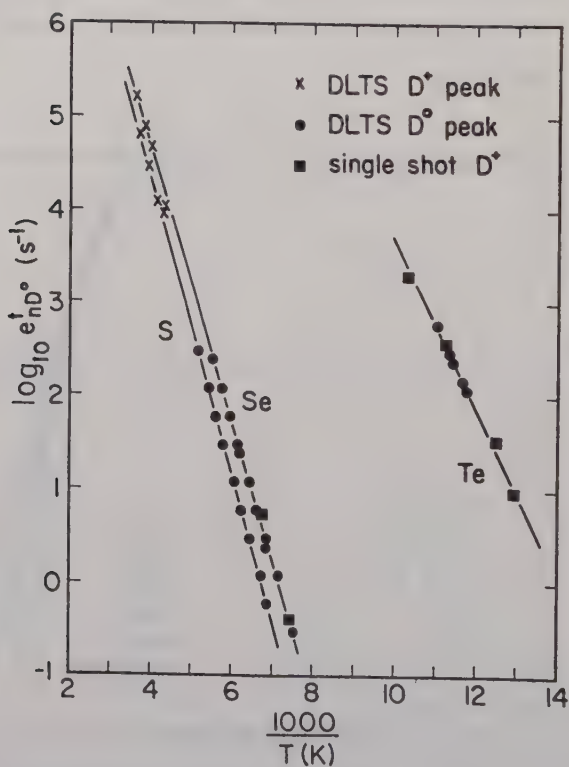


Fig.15 Comparison of thermal emission data obtained with conventional methods (full circles) and with the method explained in Fig.12 (crosses and squares).

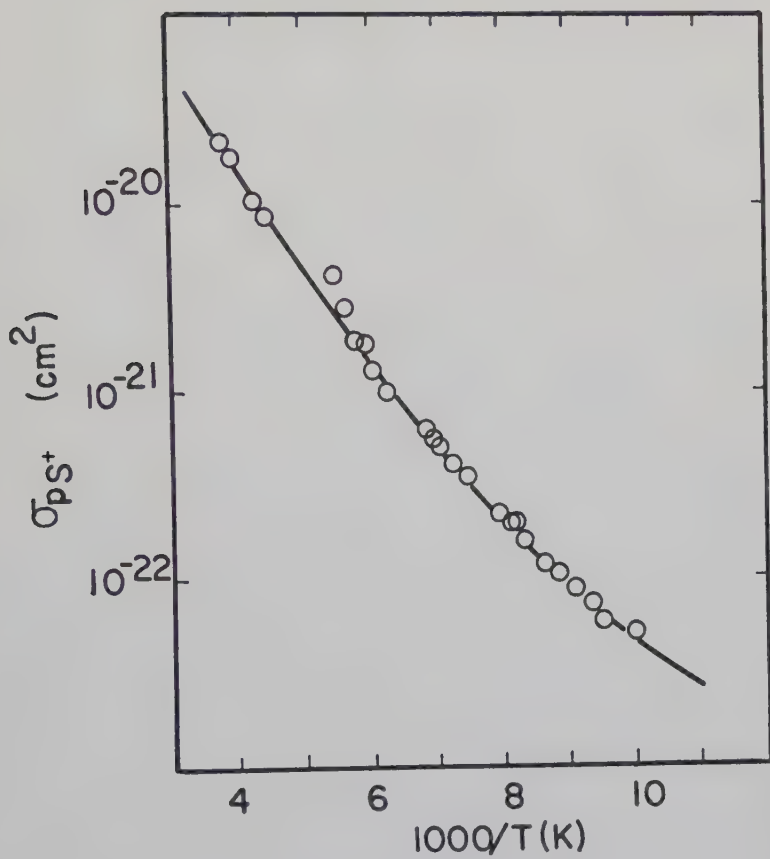


Fig.16 Hole-capture cross section of  $S^+$  (circles) fitted to the MPE model of Ref.11 (solid line).









Photothermal investigations of magnesium related donors in silicon.

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Abstract Photothermal spectra of the interstitial Mg double donor have been recorded and investigated. A strong Fano resonance structure has been observed for the singly ionized center and is discussed in some detail. In addition, two other Mg related donors with binding energies of about 55 and 93 meV respectively, have been observed.

# Photothermal investigations of magnesium related donors in silicon.

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## I Introduction

Doping silicon with magnesium gives rise to several centers<sup>1-5)</sup>. The most extensively studied Mg related center is the interstitial double donor. A double donor has three charge states: A neutral ( $D^0$ ), a singly positively ( $D^+$ ) and a doubly positively charged state ( $D^{2+}$ ). Absorption measurements of the magnesium double donor in silicon has given binding energies for the  $Mg_i^0$  and  $Mg_i^+$  centers of about 107 meV and 256 meV<sup>1,2,4)</sup>, respectively. Recently, a study of four shallow magnesium related donors has been published.<sup>3)</sup> The shallow donors have binding energies of 0.04, 0.055, 0.08 and 0.093 eV as deduced from Hall effect measurements. The energy level schemes of the excited states of  $Mg_i^0$  and  $Mg_i^+$  as well as the 0.093 eV center have been found to be well described by effective mass theory (EMT).<sup>6,8)</sup>

Silicon has six equivalent conduction band minima in the  $\langle 100 \rangle$  and equivalent directions. The ns-states of donors in silicon are therefore six-fold degenerate (excluding spin). This degeneracy is partially lifted by valley-orbit interaction. In tetrahedral ( $T_d$ ) symmetry, an s-state is split into a one-fold ns( $A_1$ ), a two-fold ns(E), and a three-fold degenerate ns( $T_2$ ) state where  $A_1$ ,  $T_2$  and E are irreducible representations of the  $T_d$  point group (Fig.1). All data available on interstitial

magnesium suggest that the local symmetry of the interstitial double donor is  $T_d$  and that the ground state is  $1s(A_1)^{2,9}$  (in contrast to the interstitial Li donor in silicon, where the ground state belongs to the  $E+T_2^{10}$  representation). According to EMT and group theory, transitions from the  $1s(A_1)$  ground state to p-states are both dipole and symmetry allowed. However, since the binding energy of  $1s(A_1)$  for  $Mg_i^0$  and  $Mg_i^+$  is much larger than predicted by EMT, the selection rules for dipole transitions may play a minor role and, hence, transitions which are symmetry allowed but dipole forbidden, such as  $1s(A_1)-ns(T_2)$  may be expected to occur. Direct transitions from  $1s(A_1)$  to  $ns(T_2)$  states in Si have been observed for  $Bi^{11}, P$  and  $As^{12}$  as well as  $S, Se$  and  $Te^{8,13}$  single substitutional donors. Similar transitions to  $ns(E)$  states, which are both symmetry and dipole forbidden have been observed for  $Si:As^{12}$ .

Additional structure above the ionization limit has been reported in several studies of both shallow centers<sup>14-16</sup> and deep chalcogen related donors in silicon<sup>17</sup>. This structure is due to a higher order process which involves intervalley phonons and is discussed in terms of Fano-resonances<sup>15,17-19</sup>. By studying these resonances it is possible to determine binding energies of states which cannot be reached by direct optical transitions from the ground state and therefore are not observed e.g. in absorption spectra.

In this paper we report on photoconductivity spectra of Mg doped silicon. The excited states are detected by a two-stage photothermal process, in which a bound charge carrier is optically excited from the ground state into an excited state



and then by thermal emission ejected into the corresponding band, thus contributing to the conductivity. The discrete line spectra of several Mg related centers are given. The Fano resonance structure of  $Mg_1^+$  has been investigated in detail.

## II Experimental details

The samples were prepared from FZ silicon single crystals with n-type phosphorus doping giving a resistivity of  $1000\Omega\text{cm}$ , and p-type boron doping corresponding to  $4\Omega\text{cm}$ , respectively. The quartz ampoules, containing the samples and the doping material, were filled with Ar at a pressure corresponding to 1 atm at the diffusion temperature and sealed. The diffusion was carried out using a sandwich technique earlier described in the literature.<sup>20)</sup> The silicon slices making up the sandwich structure were held together by a quartz clamp. The diffusion was performed at  $1200^\circ\text{C}$ , using a diffusion time of 1 hour. The samples were quenched in cold water. After sawing the samples apart, they were polished and etched. Contacts for photoconductivity measurements were made by rubbing Ga-Al onto the surface. The spectra were recorded at temperatures between 10-100K, using a Nicolet 8000HV Fourier transform spectrometer. In all of the measurements the resolution of the spectra was limited by the sample properties rather than by the instrument.

## III Results and discussion

### a) $Mg_1^0$

The photoconductivity signal of our samples exhibited a discrete line spectrum similar to those of the shallow group V donors.

The binding energy of the  $Mg_i^0$  ground state was obtained by adding the EMT binding energy of the  $4p_{\pm}$  excited state ( $2.187 \text{ meV}^{8)}$  to the experimental determined energy of the  $1s(A_1) - 4p_{\pm}$  transition giving a value of  $107.50 \text{ meV}$ . Our result is very close to the values previously reported<sup>1,2,4)</sup>. In Table I the energies of transitions from the ground state into several different excited states are presented. The resulting binding energies for the other excited states are given, as well as the calculated binding energies and the difference between the experimental and calculated binding energies for each state.

Since the EMT binding energy of the  $1s(A_1)$  state of  $31.262 \text{ meV}^{8)}$  is about 3 times smaller than the binding energy of the ground state of  $Mg_i^0$  one may assume that the ground state acts as a deep state. The dipole selection rule for the  $1s(A_1) - 1s(T_2)$  transition, which is symmetry allowed but dipole forbidden, is then expected to be less important. However, in spite of several attempts, no signal could be obtained, neither in absorption, nor photoconductivity measurements, corresponding to such a transition.

#### b) $Mg_i^+$

When ionizing the neutral double donor, the remaining electron becomes more strongly bound to the Mg atom. In Fig.2, a photoconductivity spectrum of  $Mg_i^+$  is presented. The spectrum consists of a line spectrum below the ionization limit and a part of the Fano structure above the ionization limit. The line spectrum exhibits only dipole and symmetry allowed transitions, as for the  $Mg_i^0$  spectrum. The photothermal process mentioned above favours the detection of higher excited states relative to

the lower lying states. The binding energies of the higher excited states are increased by about a factor of 4, compared to the neutral center. Using the same procedure as for the  $Mg_i^0$  center, the binding energy of the  $Mg_i^+$  ground state was determined to be 256.49 meV.

In addition to the previously reported transitions, three new lines were detected (Fig.3). Comparing our results with EMT binding energies, we conclude that they are due to the  $1s(A_1)-4f_{\pm}, 6p_{\pm}$  and the  $7p_{\pm}$  transitions. In Table II the energies of the observed transitions between the ground state and various excited states of  $Mg_i^+$  are presented. The calculated ionization energy, the resulting binding energies, the calculated binding energies and the differences between experimental and calculated binding energies are given in this case also.

In Fig.3a the part of the  $Mg_i^+$  spectrum corresponding to excitation from  $1s(A_1)$  into the conduction band is shown. These structures originate from interaction between a continuum state in the conduction band and a discrete electron-phonon state (Fig.4). This process is called a Fano resonance. As mentioned above, forbidden transitions are not to be disregarded during the designation of the resonances. Previous work<sup>17)</sup> shows that replicas of the  $ns(A_1), ns(E)$  and  $ns(T_2)$  states can be observed and that the resonances involving  $ns(A_1)$  and  $ns(T_2)$  states are strong, whereas the  $ns(E)$  resonances are weaker. The phonons involved in this process are the intervalley phonons  $gLO=63.9\text{meV}$ ,  $fTO=59.1\text{meV}$ , and  $fLA=48.1\text{meV}$ <sup>17)</sup>. It has also been shown that the fLA phonon interacts more weakly than the optical ones.<sup>21)</sup> This is also the case in the spectrum in Fig.3a. None of the structures can be explained by a fLA emission and the fLA

phonon may be excluded in the interpretation. It is also obvious from earlier experiments<sup>17)</sup> that the interaction of the fTO phonon is substantially stronger than that of the gLO phonon.

By adding the fTO energy to the known transition energies of  $\text{Mg}_1^+$  and superimposing the result onto the Fano structure, several resonances could easily be given a designation (Fig.3a). However, some dips are still impossible to account for, e.g. one strong resonance at about 257meV (below the  $2p_0 + \text{fTO}$  dip) and one at about 277meV (between the  $2p_0$  and  $2p_{\pm}$  fTO replicas). In EMT, the energy of the 2s state falls inbetween the energies of the  $2p_0$  and  $2p_{\pm}$  states. The 2s state splits into three terms just like the 1s state. The amplitude of the 2s(E) wavefunction is small at the core of the center, and accordingly the energy of the 2s(E) state is expected to be close to the 2s(EMT) value. Since neither the 257, nor the 277 meV resonance coincides with any replica given by EMT, we may rule out the possibility of the resonances being due to transitions involving 2s(E). An electron in the  $2s(A_1)$  state is much more affected by the short range potential than in the  $2s(T_2)$  state and thus  $2s(A_1)$  should have the largest binding energy of the two. The major structures are well interpreted involving only the fTO phonon. This is in agreement with the statement above of fTO giving stronger resonances than gLO. From this we interpret the 257meV and 277meV resonances to be the  $2s(A_1) + \text{fTO}$  and  $2s(T_2) + \text{fTO}$  replicas, respectively (Fig.3b). The assignment of the 257meV resonance as  $2s(A_1) + \text{fTO}$  is less certain, since it almost coincides with the ionization limit of  $\text{Mg}_1^+$  and the dip might be due to unresolved excited states.

By only taking fTO into account, we are able to identify resonances up to  $6p_{\pm} + \text{fTO}$ . In spite of this, there are some minor structures in the vicinity of  $2s(T_2) + \text{fTO}$  (see insert of Fig.3b). Considering that  $2s(E)$  is expected to be very close to  $2s(\text{EMT})$ , and by adding the fTO and gLO energies to the resulting energy of  $1s(A_1) - 2s(\text{EMT})$ , we deduce that two of the resonances may be due to  $2s(E) + \text{fTO}$  and gLO, respectively. The  $4p_0 + \text{fTO}$  and  $3p_{\pm} + \text{fTO}$  resonances fall into a rather broad dip, and it is improbable that this structure is formed by these two resonances only. None of the measured transition energies plus fTO or gLO coincide with the structure, but by invoking the EMT energies of  $3d_0$  and  $3d_{\pm}$  plus fTO, it is possible to get good agreement (Fig.3b).  $2p_0 + \text{fTO}$  and  $2p_{\pm} + \text{fTO}$  almost coincide with the center of the resonance dip. This is not the case for  $3p_0 + \text{fTO}$ , and it is reasonable to assume that another state is resonant at almost the same energy. For 3s-states it is possible to estimate the binding energies from the knowledge of the binding energies of the valley-orbit split 2s-states if they do not strongly deviate from EMT, using a scaling procedure.<sup>7)</sup> By scaling and adding the fTO energy we found that the  $3s(A_1)$  and the  $3s(T_2)$  resonances should coincide with the resonances originating from  $2p_{\pm}$  and  $3p_0$ , respectively. Since the  $2s(T_2)$ -related resonance is comparatively strong, we expect that  $3s(T_2)$  is involved in the broadening of the  $3p_0 + \text{fTO}$  resonance dip. In Fig.3b the resonances that have been given a designation using other methods than adding the fTO phonon energy to known transition energies are shown. These designations are of course less certain than the ones in Fig.3a.



### c) Mg related complexes

There has been some indication of Mg forming complexes with other impurities.<sup>3)</sup> We have recorded photoconductivity spectra of two neutral donors, one with an ionization energy of 55 meV and one at 93 meV. These binding energies coincide with previously reported binding energies for Mg related centers<sup>3)</sup>. In Fig.5 the photoconductivity spectrum of the 55 meV donor is presented. In our case, the complexes only appear in the samples that were p-type before Mg diffusion. In Table III, the energies of transitions from the ground state into some of the excited states are given for both centers. The comparison with EMT is given here also. The ionization energies have been calculated by adding the corresponding calculated binding energies to the  $1s(A_1)-4p_{\pm}$  transition energy for the 55 meV center and the  $1s(A_1)-3p_0$  energy for the 93 meV center.

### IV Conclusions

Data have been presented that show that electron-phonon interaction ( Fano-resonances ), earlier reported for many substitutional centers in silicon, are also observed for interstitial centers, such as the Mg double donor. A new Mg related donor with an activation energy of 55 meV has been studied and its energy level scheme has been found to agree with EMT.

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TABLE I  
 $\text{Mg}_1^0$   
 (The energies are given in meV.)

| Transition<br>( $1s(A_1) -$ ) | Energy | Binding energy ( $E_B$ ) | $E_B$ EMT | $E_B(\text{exp}) - E_B(\text{EMT})$ |
|-------------------------------|--------|--------------------------|-----------|-------------------------------------|
| $2p_0$                        | 95.82  | 11.68                    | 11.492    | 0.19                                |
| $2p_{\pm}$                    | 101.20 | 6.30                     | 6.402     | -0.10                               |
| $3p_0$                        | 101.94 | 5.56                     | 5.485     | 0.08                                |
| $3p_{\pm}$                    | 104.42 | 3.08                     | 3.120     | -0.04                               |
| $4p_{\pm}$                    | 105.31 | 2.19                     | 2.187     | 0                                   |
| $E_I$                         | 107.50 |                          | 31.262    |                                     |

TABLE II  
 $\text{Mg}_i^+$   
 (The energies are given in meV).

| Transition<br>$1s(A_1) -$ | Energy | Binding energy ( $E_B$ ) | $E_B$ EMT | $E_B(\text{exp}) - E_B(\text{EMT})$ |
|---------------------------|--------|--------------------------|-----------|-------------------------------------|
| $2s(A_1)^a$               |        | 59.2                     | 35.424    | 23.7                                |
| $2s(T_2)^a$               |        | 38.9                     | 35.424    | 3.5                                 |
| $2p_0^b$                  | 208.63 | 47.87                    | 45.968    | 1.90                                |
| $2p_{\pm}$                | 230.32 | 26.18                    | 25.608    | 0.57                                |
| $3p_0$                    | 233.82 | 22.68                    | 21.940    | 0.74                                |
| $3p_{\pm}$                | 243.92 | 12.58                    | 12.480    | 0.10                                |
| $4p_{\pm}$                | 247.75 | 8.75                     | 8.748     | 0                                   |
| $4f_{\pm}$                | 249.09 | 7.41                     | 7.576     | -0.17                               |
| $5p_{\pm}$                | 250.71 | 5.79                     | 5.796     | -0.01                               |
| $6p_{\pm}$                | 252.37 | 4.13                     | 4.280     | -0.15                               |
| $7p_{\pm}^c$              | 253.45 | 3.06                     | 3.288     | -0.23                               |
| $E_I$                     | 256.50 |                          | 31.262    |                                     |

a) The binding energies are obtained from Fano resonances.

b) From ref.2.

c) The assignment  $7p_{\pm}$  and the transition energy are less certain.

TABLE III  
Mg related donors  
(The energies are given in meV.)

| Transition<br>( $1s(A_1) -$ ) | Energy | Binding energy ( $E_B$ ) | $E_B$ EMT |
|-------------------------------|--------|--------------------------|-----------|
| $2p_{\pm}$                    | 48.91  | 6.38                     | 6.402     |
| $3p_{\pm}$                    | 52.16  | 3.13                     | 3.120     |
| $4p_{\pm}$                    | 53.10  | 2.19                     | 2.187     |
| $E_I$                         | 55.29  |                          |           |
| $2p_0$                        | 81.96  | 11.44                    | 11.492    |
| $2p_{\pm}$                    | 87.23  | 6.17                     | 6.402     |
| $3p_0$                        | 87.92  | 5.49                     | 5.485     |
| $E_I$                         | 93.40  |                          |           |



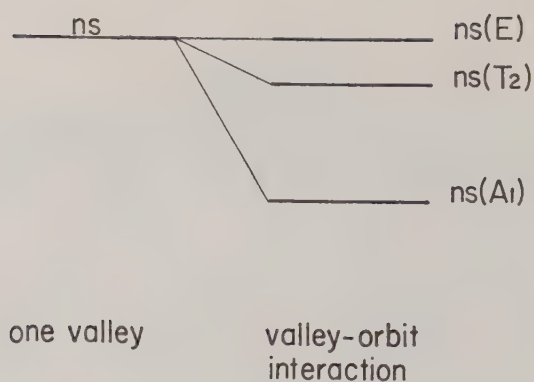


Fig.1 The valley-orbit splitting of an s-state of a donor in Si in  $T_d$  symmetry.

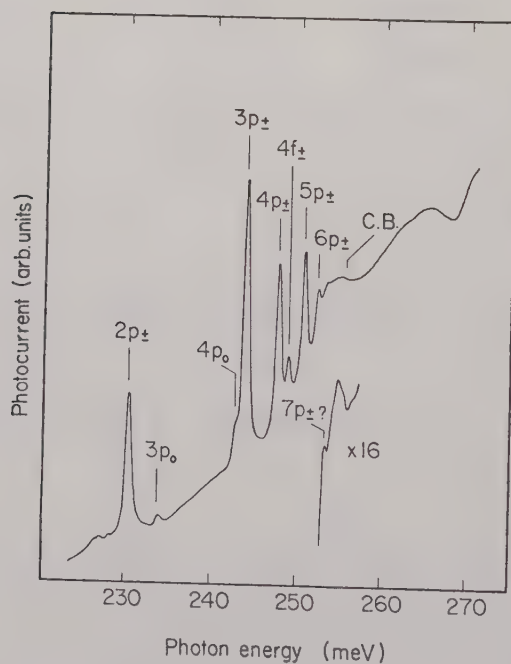
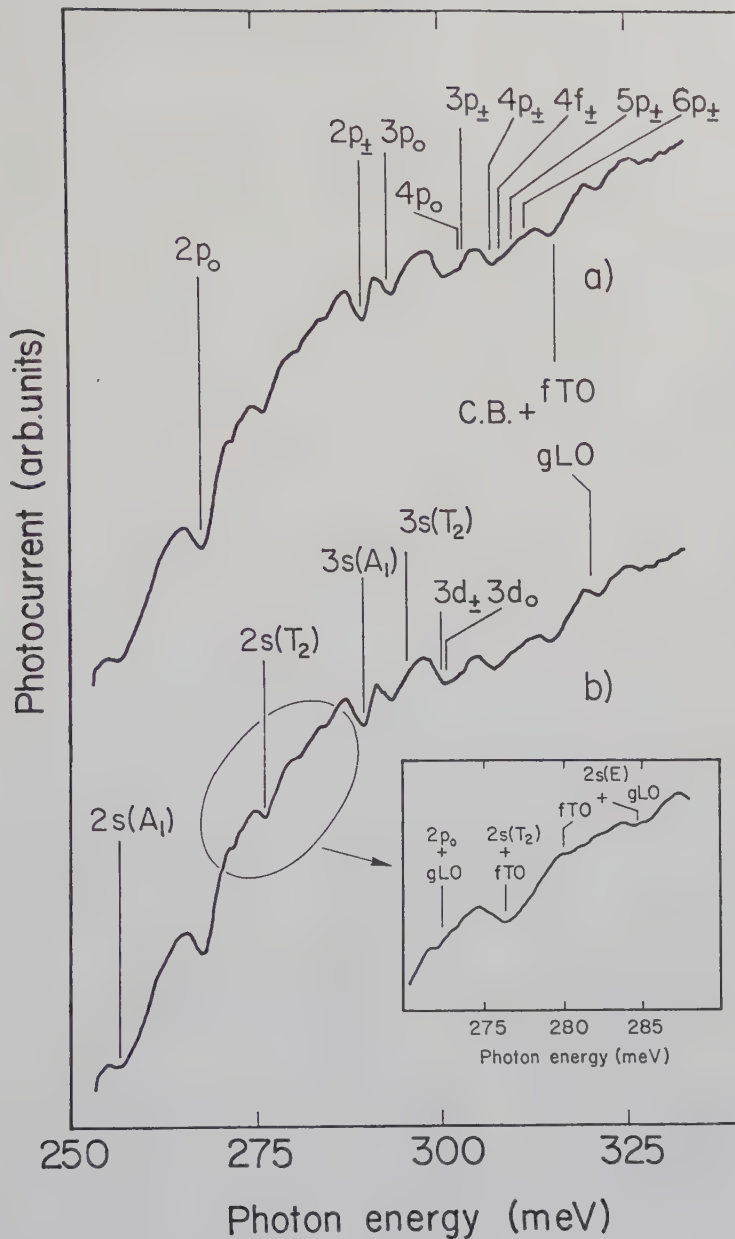


Fig.2 The photoconductivity spectrum of  $Mg_i^+$ . The assignment "7p<sub>±</sub>" is less certain.



**Fig.3** The photoconductivity spectrum of  $\text{Mg}_1^+$  above the ionization limit, showing the Fano resonance structure.

a) The fTO phonon energy has been added to observed transition energies.

b) Interpretation of additional Fano structure using other methods than in a). The phonon energy used in the interpretation is the energy of fTO, unless stated otherwise.

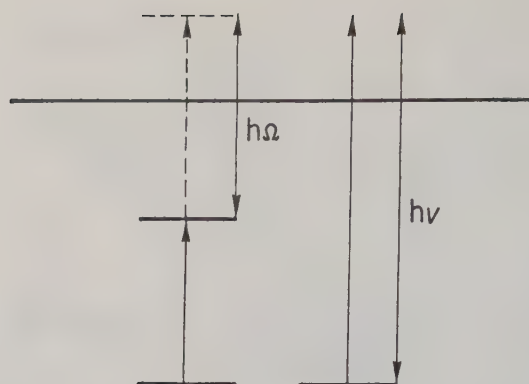


Fig.4 The Fano resonance process.

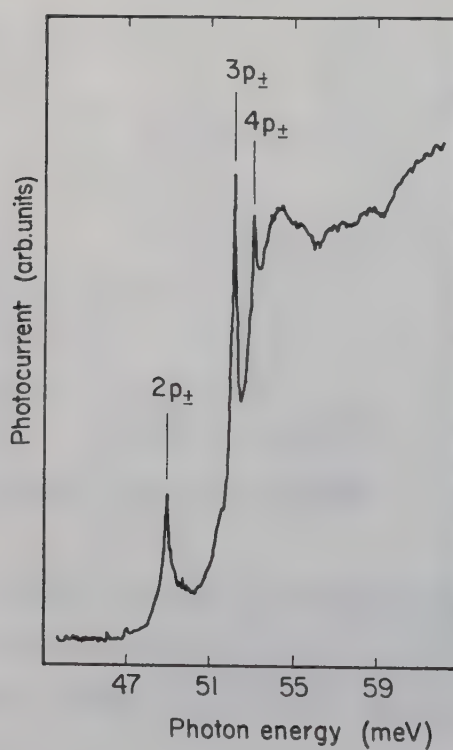


Fig.5 Photoconductivity spectrum of a Mg related donor with a binding energy of about 55 meV.







Absorbtion Study on Beryllium Doped Silicon.

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Abstract

Absorbtion studies on beryllium doped silicon reveals three acceptor centers with binding energies of about 192, 200, and 93 meV. The line spectra are similar to the ones observed for the group III acceptors. In addition to the  $P_{3/2}$  line spectra a  $P_{1/2}$  line spectra and Fano-resonance structures have been studied for the 192 meV center. The nature of previously reported Be and Be-Li related centers is discussed in terms of X-acceptors.

## Absorbtion Study on Beryllium Doped Silicon.

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### I. Introduction

Absorbtion<sup>1</sup> and photothermal<sup>2,3</sup> studies of group III acceptors in silicon have been very successfull in investigating bound to bound hole excitation processes. Using effective mass theory<sup>4,5</sup> (EMT) theoretical studies have given binding energies of the bound states in close agreement with experimental data. The degeneracy at the top of the valence band in silicon is partly lifted by the spin-orbit interaction into two bands ( $P_{3/2}$  and  $P_{1/2}$ ) seperated by the spin-orbit energy<sup>6</sup>  $\Delta_{so} = 42.62$  meV (Fig.1). Therefore, in first approximation, EMT predicts that the bound states are seperated into two series of states: one originating from the  $P_{3/2}$  and one from the  $P_{1/2}$  valence band, without any mixing of states from different bands. This approximation is only valid if  $\Delta_{so}$  considerably exceeds the binding energies of the bound states, which is not the case in Si.

Electron-phonon interactions are expected to be weak in Si. This may be the reason why only no-phonon bound-to-bound transitions have been reported. Nevertheless, interactions with phonons have been observed through resonance processes. When transition energies from the ground

to excited states coincide with some proper phonon energy, resonance effects may occur leading to a substantial broadening of e.g. absorption lines<sup>7-9</sup>. Resonances between discrete and continuum electron/hole-states in silicon have been observed experimentally for the group III acceptors<sup>10,11</sup>, group V donors<sup>11,12</sup>, interstitial Mg double donor<sup>13</sup>, and chalcogen related donors<sup>14,15</sup>. They are discussed in terms of Fano-resonances and are observed as additional structure in the continuum part of the spectra.

Beryllium, a group II element, gives rise to several acceptor centers<sup>15-18</sup> when incorporated into silicon. Absorption measurements have shown line spectra of two Be related acceptors with ground state binding energies of about 192 meV (BeI) and 145 meV (BeII). The hole excitation spectra from the ground state to excited states reveal a line structure similar to the one of the group III acceptors. Since substitutional Be may accept two electrons in order to complete the  $sp^3$  hybrid orbitals it is expected that beryllium on substitutional site acts as a double acceptor. However, no line spectra corresponding to a singly ionized center have hitherto been reported in literature. Acceptor line spectra of Be-Li complexes have also been studied<sup>17</sup>. The binding energies of these complexes are about 106 meV and 81 meV.

The purpose of this paper is to report new data on the  $P_{3/2}$  and  $P_{1/2}$  line spectra of the BeI center including a Fano resonance structure. In addition, absorption data on two new Be related acceptor centers are presented and the origin of some Be related acceptors previously observed is discussed.

## II. Experimental details

High purity phosphorus doped silicon with low O and C concentrations, and resistivities of 1000  $\Omega\text{cm}$  (sample#1) and 24-28  $\Omega\text{cm}$  (sample#2) have been used in this study. Be was evaporated onto the polished and etched ( $\text{HF} + \text{HNO}_3$ ) surfaces of the samples. The samples were diffused in an evacuated and sealed quartz ampoule and heat treated in 1250 $^{\circ}\text{C}$  (5 min) and 1000 $^{\circ}\text{C}$  (1 h). After quenching in air the samples have been etched ( $\text{HF} + \text{HNO}_3$ ) in order to obtain surfaces of high optical quality. The absorption measurements were performed with a Nicolet 8000 HV Fourier transform spectrometer.

## III. Results and discussion

Fig.2a shows the absorption spectrum obtained from a measurement on sample#1 of a Be related acceptor. From the line spectrum a binding energy of about 192 meV is deduced. The center is identified as the BeI acceptor previously reported. Below the continuum of the  $\text{P}_{3/2}$  valence band 5 lines are observed. An additional line (4') appears slightly above the  $\text{P}_{3/2}$  ionization limit. Furthermore a low energy partner (3') of line 4' is found when the signal is scaled up (see insert in Fig.2a). The energy differences between line 2', 3', and 4' are very close to the corresponding energy differences between line 2, 3, and 4 and it is therefore concluded that lines 2', 3', and 4' belong to a different acceptor center, which we label BeIII. This interpretation is further confirmed by comparing the intensities of corresponding lines obtained in sample#2 (Fig.2b) and sample#1 (Fig.2a). The intensities of lines 2' and 4' and lines 2 and 4 in Fig.2b are similar in contrast to the result shown in Fig.2a suggesting that the two series of lines originate from two different

centers. In Table I the binding energies and the labels of the hole states involved in the transitions are presented and compared with corresponding boron and theoretical values. The ground state binding energies are calculated by adding the theoretical binding energy of line 4 to the measured energy of this line.

Yet another Beryllium related center (BeIV) has been observed in sample#1 in addition to the two Be centers (BeI and BeIII) already mentioned. Three lines are observed (Fig.3). The binding energies of states corresponding to these lines as well as the calculated ground state energy of the center are presented in TableI.

It was already mentioned in the introduction that a second series of bound states originating from the  $P_{1/2}$  valence band has been observed for group III acceptors in silicon. In Fig.4 a series of  $P_{1/2}$  lines detected in sample #1 is presented. The intensity of the BeI absorption lines is much higher than for corresponding lines of the BeIII center in this sample. Since the energy difference of 42.81meV between line A (Fig.4) and line 4 (Fig.2a) almost equals the difference between the  $2p'$  line and line 4 for boron (43.26 meV)<sup>1</sup> we identify our line A to be the  $2p'$  line of BeI. The ionization limit of the  $P_{1/2}$  of BeI is calculated by adding  $\Delta_{so}$  to the ionization limit of the  $P_{3/2}$  series. The energy position of line C (Fig.4) is clearly above the  $P_{1/2}$  ionization limit of BeI. Since a  $2p'$  line is expected to have the highest intensity, we believe that line C is the  $2p'$  line of BeIII. Line B in Fig.4 appears 4.45 meV above  $2p'$ (BeI). The structure is rather broad and no definite assignment can therefore be made for line B. It is, however, not unreasonable to believe that line B involves both the  $3p'$  and  $4p'$  line of BeI, since the energy differences  $2p' - 3p'$  and  $2p' - 4p'$  for the group III acceptors are



about 3 and 4 meV respectively<sup>1</sup>.

Above the  $P_{1/2}$  ionization limit a structure is observed (Fig.5) which we believe is due to Fano-resonances. Comparing the energy difference of the two major Fano dips with the energy difference between the absorption lines 1 and 2 of BeI it is concluded that the resonances may involve states causing line 1 and 2 of BeI. The phonon involved is the  $O^{\Gamma}$  with an energy of 64.5 meV<sup>19</sup> ( $519.9 \text{ cm}^{-1}$ ). The energies indicated by arrows in Fig.5 are obtained by adding the  $O^{\Gamma}$  energy to the energies of the observed transitions from the ground state into the states causing line 1 and 2. Above the line 2 +  $O^{\Gamma}$  dip a minor structure is observed which may result from Fano resonances involving line 3 and 4 of BeI.

The defect structure of the three Beryllium related acceptor centers is not known. However, in some previously reported absorption studies on Be doped silicon, the BeI center was observed together with a second acceptor (BeII) of about the same concentration as BeI. The ground state binding energy of BeII was reported to be about 146 meV. In addition two Be-Li complexes have been observed. Recently it has been shown that group III acceptors have associated acceptors with smaller ionization energies, the so called X-acceptors. The origin of the X-acceptors has been studied both experimentally<sup>20, 21</sup> and theoretically<sup>21, 22</sup>. It could be shown that the X-acceptor concentrations depend on the carbon concentration and also that carbon is the only group IV element which causes X-centers with smaller binding energies<sup>22</sup> of the ground state than those of the original acceptor. The C concentration in our samples is believed to be very low and this may be the reason why we did not observe the BeII center. Using the results of Ref.22, an ionization energy of about 138 meV for

the BeI related X-acceptor can be estimated. Comparing this value with the actual observed energy of the BeI partner, 146 meV, supports our suggested interpretation of BeII as being an X-acceptor to BeI. Furthermore, the Be-Li complexes in Ref.17 may also be discussed in terms of an acceptor - X-acceptor pair. The binding energies of the Be-Li complexes are about 106 and 81 meV. The estimated binding energy of the X-acceptor related to the 106 meV center is about 75 meV and the result is once again in good agreement with the observed value.

#### IV Summary

The  $P_{3/2}$  line spectra of three Be related acceptor centers have been studied. The binding energy of these centers (BeI, BeIII, and BeIV) was determined to be 192.08 , 199.61, and 92.60 meV, respectively. Although, the ground state is much deeper than predicted by EMT, the binding energy of the excited states are well described by EMT. Excitations from the  $P_{3/2}$  ground state to resonant  $P_{1/2}$  states have been observed for BeI and BeIII. Fano resonance structures of BeI have been studied and as in the case of groupIII acceptors the phonon involved has been found to be  $O^I$

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TABLE I

| Transition<br>$1S_{3/2}^-$ | BeI    | BeIII  | BeIV   | B <sup>*</sup> | Theory <sup>**</sup> |
|----------------------------|--------|--------|--------|----------------|----------------------|
| 1 $2P_{3/2}$               | 15.30  | -      | (14.5) | 15.33          | 15.5                 |
| 2 $2P_{5/2}(\Gamma_8^-)$   | 11.28  | 11.31  | 11.18  | 11.18          | 11.4                 |
| 3 $3P_{3/2}$               | 7.35   | (7.0)  | -      | 7.36           | 7.3                  |
| 4 $2P_{5/2}(\Gamma_8^-)$   | 6.1    | 6.1    | 6.1    | 6.1            | 6.1                  |
| $E_B$                      | 192.08 | 199.61 | 92.60  | 45.71          |                      |

Figures in parenthesis are less certain.

<sup>\*</sup>) from ref.7

<sup>\*\*</sup>) from ref.4



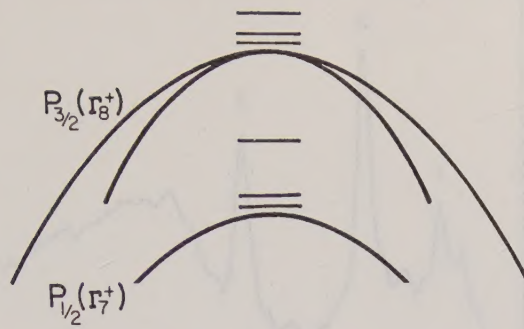


Fig.1 A simplified figure showing the top of the valence band in Si.

The spin-orbit interaction splits the band into an upper  $P_{3/2}$  and a lower  $P_{1/2}$  band. Bound and resonant acceptor states are indicated.

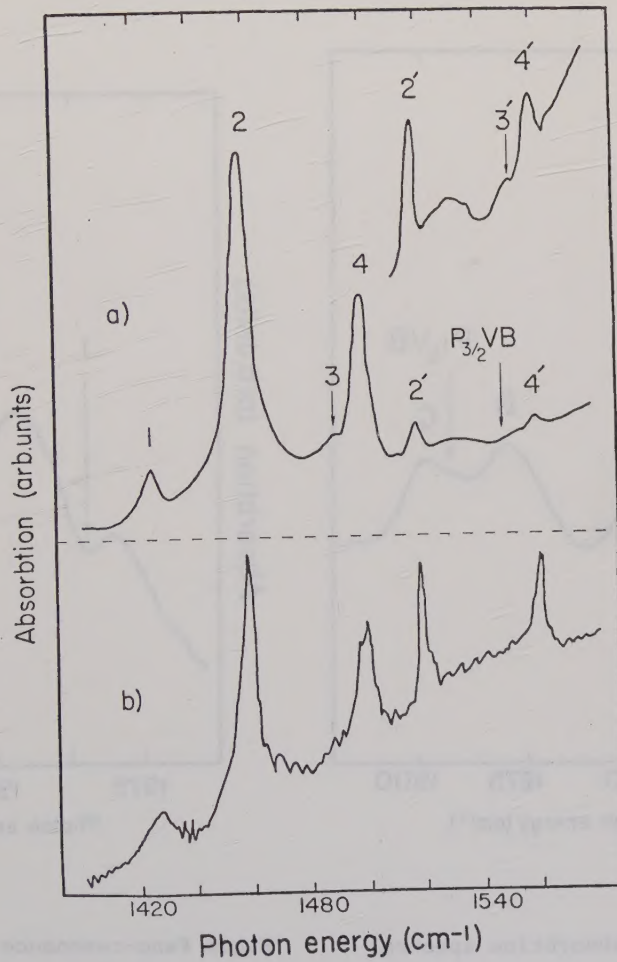


Fig.2 Absorption spectra showing the  $P_{3/2}$  line spectra of BeI and BeIII.

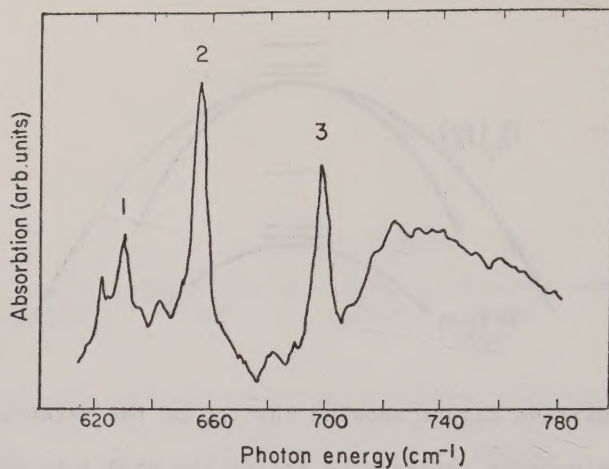


Fig.3 Absorption spectrum of Be IV.

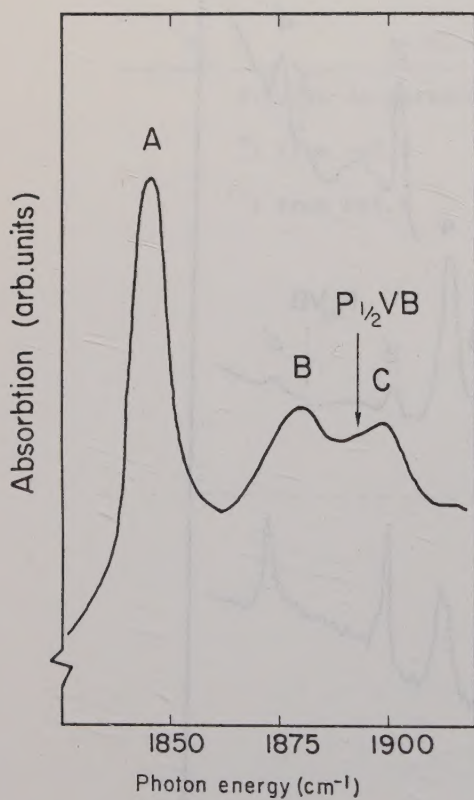


Fig.4  $P_{1/2}$  absorption spectra.

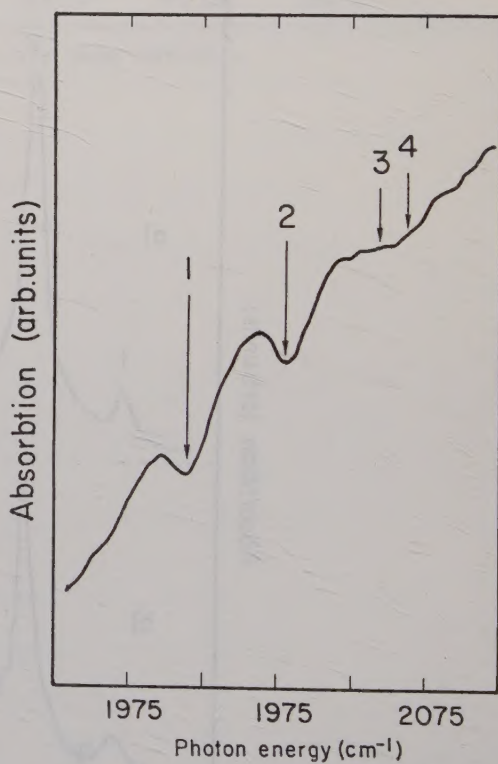


Fig.5 Fano-resonance structures observed in sample#1.



